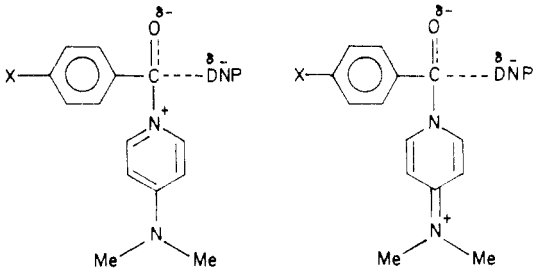
Activation Parameters. Table IV shows the activation parameters found for the reactions of DNPCB (this work) and DNPB[9] with two substituted pyridines. The large negative $\Delta S^{\ddagger}$ values for the reactions of 4-(dimethylamino)pyridine (DMAP) can be accounted for by assuming that I and II (X = H, Cl) are the two main canonical

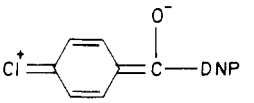


I II

structures of the hybrid transition state of the second step of eq 4. Contribution of a canonical structure analogous to II to the ground-state DMAP should be smaller than the contribution of II to the hybrid transition state since the former involves total charge separation among the two nitrogen atoms. The loss of both rotational degrees of freedom and resonance in going from reactants to II, and the fact that the cationic amine nitrogen of II should be more solvated than the pyridine one of I (for steric reasons, due to the proximity of the latter to the acyl aryl group) explains the large negative $\Delta S^{\ddagger}$ values for the reactions of DMAP.[9]

The reactions of DNPCB and DNPB with 3-methylpyridine (MP) show less negative $\Delta S^{\ddagger}$ values (Table IV) since with MP no contribution of structures similar to II are possible.

The lower (more negative) $\Delta S^{\ddagger}$ value found in the reaction of DMAP with DNPB compared to the reaction with DNPCB (Table IV) can be explained by the assumption that the canonical structure III contributes to the hybrid of DNPCB. The contribution of the analogous



III

structure to the hybrid transition state for the DNPCB reaction should be smaller than in the ground state of DNPCB since it is known that the electronic effects of a group attached to a tetrahedral intermediate are mainly inductive.[17] Although the central carbon atom of the transition state is not exactly tetrahedral, the fact the tetrahedral intermediate involved in the reaction (eq 4) is very reactive implies that the above carbon atom has a strong tetrahedral character, according to the Hammond postulate.[18] The high polarity, and therefore large solvation (by polar solvents) of III, and the fact that a structure like III is negligible in the hybrid DNPB molecule, should be responsible for the higher (less negative) $\Delta S^{\ddagger}$ value found for the reaction of DNPCB.

The contribution of **II** to the hybrid transition state for the above reactions should be larger for X = Cl, in view of the value for the electron-withdrawing inductive effect of Cl ($\sigma_I = 0.47$),[16] which should favor that structure relative to I. This fact should lead to a higher $\Delta S^{\ddagger}$ for the reaction of DMAP with DNPB compared to that with DNPCB. The fact that $\Delta S^{\ddagger}$ is higher for the latter reaction (Table IV) means that the effect just mentioned is smaller than that discussed above regarding the contribution of III to the ground state of DNPCB.

Acknowledgment. We thank D.I.U.C. (Dirección Investigación Universidad Católica de Chile) for financial support of this work.

Registry No. 2,4-Dinitrophenyl *p*-chlorobenzoate, 32792-54-4; 3-chloropyridine, 626-60-8; 3-carbamoylpyridine, 98-92-0; pyridine, 110-86-1; 3-methylpyridine, 108-99-6; 4-methylpyridine, 108-89-4; 3,4-dimethylpyridine, 583-58-4; 4-aminopyridine, 504-24-5; 4-(dimethylamino)pyridine, 1122-58-3.

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Reduction of Ketones by Tributyltin Hydride: The Effect of High Pressure on Steric Hindrance and Rearrangement Processes

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The reduction of sterically hindered ketones by tributyltin hydride under high pressure (1 GPa) afforded the corresponding alcohols in good yields without the need of free radical initiator or Lewis acid catalyst. Cyclopropyl ketones and α,β-epoxy ketones were also reduced in high yields under 1400 MPa with preservation of the three-membered ring.

The addition of tributyltin hydride to ketones is a well-known reaction that leads after protonolysis to the corresponding alcohols (Scheme I). A free radical mechanism is involved when the reaction is performed in the presence of azobisisobutyronitrile (AIBN), UV light, etc. Intermediate ionic species have to be considered when the addition is achieved in polar solvents or under Lewis acid catalysis.[1]

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Scheme I

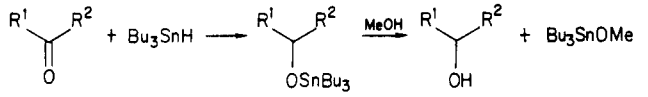
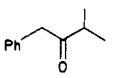
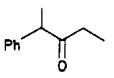
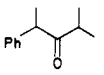
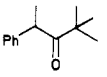


Table I. Reduction of Ketones Substituted with Groups of Different Bulks

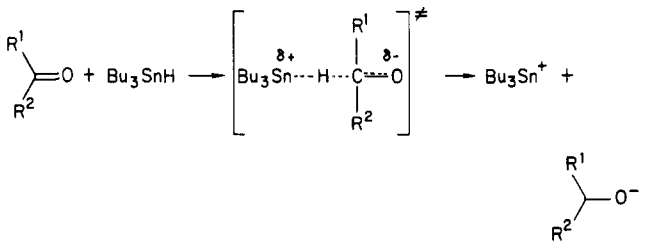
expt	ketones[a]	% yields in alcohols[b] 0.1 MPa	1000 MPa	yield ratio
1		35[c]	64[d]	1.8
2		18	64	3.5
3		15	58	3.8
4		12[e]	68	5.6
5		4	62[d]	15.5
6		2	63[d]	31.5
7		0	57[d]	

[a] [Ketone] = [Bu_3SnH] ≃ 3 M in absolute methanol. [b] All the reactions were run at 55 °C during 24 h in a Teflon cell. Yields were obtained from GC analysis. [c] See ref 3a. [d] See ref 6a. [e] See ref 2a.

However, results from the literature show that steric hindrance is a major limitation to preparative purposes[2a,3a] and tributyltin triflate catalysis has been proposed recently to overcome this difficulty.[4] On the other hand, the high-pressure technique is known for its ability to overcome steric strains.[5] As an extension of our earlier work on the addition of tributyltin hydride to unsaturated systems[6] we have examined the reactions, under high pressure and neutral conditions, of a series of sterically hindered ketones. A strong facilitation of the addition was observed which can be explained in terms of kinetic effects as proposed by le Noble for the Menschutkin reaction.[5]

Since the rearrangement of intermediate radicals can be an undesirable process during the free radical stannane-mediated reduction of ketones,[7] reactions of cyclopropyl and α,β-epoxy ketones susceptible to ring-opening rearrangements have been investigated. A beneficial effect of the high-pressure technique is a predominant ring conservation.

Scheme II



Scheme III

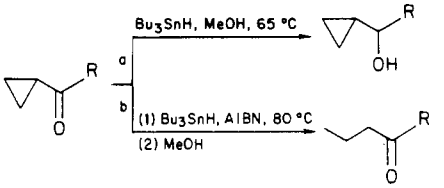


Table II. Diastereomeric Ratios for Alkyl(1-phenylethyl)carbinol[a]

R	erythro/threo ratios for PhCH(Me)CHOHR 0.1 MPa	1000 MPa
R = Et (expt 4)	0.47	0.43
R = *i*-Pr (expt 6)	0.43	0.43
R = *t*-Bu (expt 7)		0.14

[a] See Table I for yields and experimental conditions.

Results and Discussion

Reduction of Sterically Hindered Ketones. To observe the influence of pressure, the hydrostannation of ketones bearing substituents of increasing bulk has been performed in methanol as solvent under both classical conditions (0.1 MPa, 55 °C, 24 h) and high-pressure conditions (1000 MPa, 55 °C, 24 h). The results are gathered in Table I. Under 0.1 MPa (atmospheric pressure), the yields decreased from 35% (experiment 1) to 2% (experiment 6) as the bulk of the substituents increased.[8] With even greater hindrance, no reduction at all was observed (experiment 7). Parallel experiments, carried out under 1000 MPa, gave yields from 57% to 68%.

A useful parameter is the ratio between the yields at 1000 and at 0.1 MPa. This ratio expresses the acceleration effect of the pressure on the addition step. It is clear from Table I that the largest values are observed with the bulkiest substituents (for example, experiments 6 and 7). A similar trend has been observed for the Menschutkin reaction and le Noble's rationale for the latter can be extended to the hydrostannation of ketones in the following way.[5a,b] In a polar solvent such as methanol, the ionic mechanism is very likely to occur. Moreover the high pressure will also favor charge separation in the transition state[9] (Scheme II). As a consequence of the Hammond postulate, sterically hindered ketones should lead to late transition states, close to the ionic species. The electrostriction of these activated complexes will lead to very negative volumes of activation,[5a,b] and the pressure will induce large rate acceleration as defined by the rate pressure dependency $(\partial \ln k/\partial P)_T = -\Delta V^{\ddagger}/RT$.

On the other hand, from a stereochemical point of view, experiments 4, 6, and 7 provide some information concerning acyclic ketones. No significant changes were ob-

(1) Poller, R. C. *The Chemistry of Organotin Compounds*; Academic: New York, 1970; p 117.
(2) (a) Quintard, J. P.; Pereyre, M. *J. Organomet. Chem.* **1974**, *82*, 103. (b) Zushi, S.; Kodama, Y.; Fukuda, Y.; Nishihata, K.; Nishio, M.; Hirota, M.; Uzawa, J. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2113.
(3) (a) Quintard, J. P.; Pereyre, M. *Bull. Soc. Chim. Fr.* **1972**, 1950. (b) Hardyer, R. J.; Wicker, R. J. *J. Am. Chem. Soc.* **1958**, *80*, 640.
(4) Xian, Y. T.; Four, P.; Guibe, F.; Balavoine, G. *Nouv. J. Chim.* **1984**, *8*, 611.
(5) (a) le Noble, W. J.; Asano, T. *J. Am. Chem. Soc.* **1975**, *97*, 1778. (b) le Noble, W. J.; Kelm, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 841. (c) Jenner, G. *J. Chem. Soc., Faraday Trans. 1*, in press.
(6) (a) Rahm, A.; Degueil-Castaing, M.; Pereyre, M. *J. Organomet. Chem.* **1982**, *232*, C29. (b) Degueil-Castaing, M. Thesis, Bordeaux, 1983. (c) Rahm, A.; Degueil-Castaing, M.; Pereyre, M. *Int. Conf. Organomet. Coord. Chem. Germanium, Tin Lead, 4th* **1983**.
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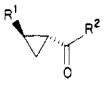
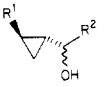
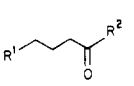
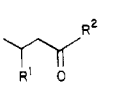
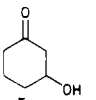
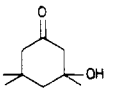
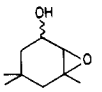
(8) Taft, R. W. *J. Am. Chem. Soc.* **1952**, *74*, 3120.
(9) Degueil-Castaing, M.; Rahm, A.; Maillard, B. *J. Organomet. Chem.* **1985**, *287*, 49.

Table III. Reduction of Cyclopropyl Ketones by Tributyltin Hydride

expt		conditions[a]	% composition of mixtures[d] 			% overall yield
8						
A	R^1 = H, R^2 = Me	1400 MPa, 55 °C	100			99
B		0.1 MPa, 55 °C		1		1
C		0.1 MPa, AIBN, 80 °C			100	85
9						
A	R^1 = H, R^2 = Ph	1500 MPa, 60 °C	87	13		40
B		0.1 MPa, 60 °C	<0.5	<0.5		<1
C		0.1 MPa, AIBN, 80 °C			100	90
10						
A	R^1 = Me, R^2 = *i*-Pr	1400 MPa, 55 °C	100			97
B		0.1 MPa, 55 °C	<0.5	<0.5	<0.5	<1.5
C		0.1 MPa, AIBN, 80 °C		35	65	60
11						
A	R^1R^2 = $(CH_2)_3$	1400 MPa, 55 °C	94[b]		6	99
B		0.1 MPa, 55 °C	42[c]		58	7
C		0.1 MPa, AIBN, 80 °C			100	80

[a] Noninitiated reaction, 24 h; initiated reaction; 12 h. [b] Cis/trans = 0.54. [c] Only cis alcohol. [d] GC analysis after methanolysis.

Table IV. Reduction of α,β-Epoxy Ketones by Tributyltin Hydride

expt		conditions[a]	% composition of mixtures[b] 			% overall yield
12						
A		1400 MPa, 60 °C, neat		2	98	88
B		0.1 MPa, 60 °C, neat		30	70	9
C		0.1 MPa, AIBN, 80 °C, neat	51	49		85
13						
A		1400 MPa, 60 °C, ether	1	5	94[c]	98
B		0.1 MPa, 60 °C, ether	26	10	64[d]	37
C		0.1 MPa, AIBN, 80 °C, ether	90	10		62
14						
A		1400 MPa, 60 °C, ether	1	19	80[e]	97
B		0.1 MPa, 60 °C, ether			100[f]	18
C		0.1 MPa, AIBN, 80 °C, ether	93	7		64

[a] Reaction time, 24 h. [b] GC analysis after methanolysis. [c] Cis/trans ratio = 9/91. [d] Cis/trans ratio = 7/93. [e] Cis/trans ratio = 19/81. [f] Cis/trans ratio = 12/88.

served in the diastereoisomeric ratios although the pressure was changed dramatically (Table II). In the case of 3,3,5-trimethylcyclohexanone (experiment 1) the cis/trans ratio for the corresponding alcohols increased from 0.1 at atmospheric pressure to 0.25 at 1000 MPa. Thus the classical models for asymetric induction seem to be still valid under high-pressure conditions.[2a,3a,10]

Reduction of Cyclopropyl Ketones. As mentioned above, the polar hydrostannation is the most likely mechanism for the reduction of ketones under pressure in the presence of methanol. With neat reagents the possibility of a free radical reaction pathway has to be considered and cyclopropyl ketones are a good mechanistic probe for the process involved in the hydrostannation step (Scheme III).[7] Indeed, phenyl cyclopropyl ketone reduction by tributyltin hydride under 1400 MPa led exclusively to phenylcyclopropylcarbinol when performed in the presence of methanol (reaction path a) and to a mixture of cyclopropylcarbinol and acyclic ketone (reaction path a and b) when achieved with neat reagents and in the absence of radical initiator or Lewis catalyst. These latter experimental conditions have been used for a series of differently substituted cyclopropyl ketones, and the comparative results are gathered in Table III.

Here again, the high-pressure technique led to excellent yields. Alkylcyclopropylcarbinols are by far the major and sometimes the unique products of reduction. Under atmospheric pressure (neat reagents, no radical initiator), only traces of opened reaction products were obtained (experiments 8B–11B). In the presence of the free radical initiator (experiments 8C–11C) only ring-opened products were obtained as expected from other reports.[7]

As mentioned in the previous paragraph the high-pressure favors the ionic pathway, the rate of which is dramatically increased as a consequence of the electrostriction, but experiments 9A and 11A clearly indicate that a radical reaction path is also possible (Scheme IV). However, the amount of opened products is not necessarily indicative of the extent of the radical mechanism since path d, which implies a carbon–carbon bond breaking ($\Delta V^{\ddagger} > 0$) could be strongly impeded by high pressure. This

(10) (a) Cherest, M.; Felkin, H.; Prudent, N. *Tetrahedron Lett.* **1968**, 2199. (b) Gault, Y.; Felkin, H. *Bull. Soc. Chim. Fr.* **1965**, 742.

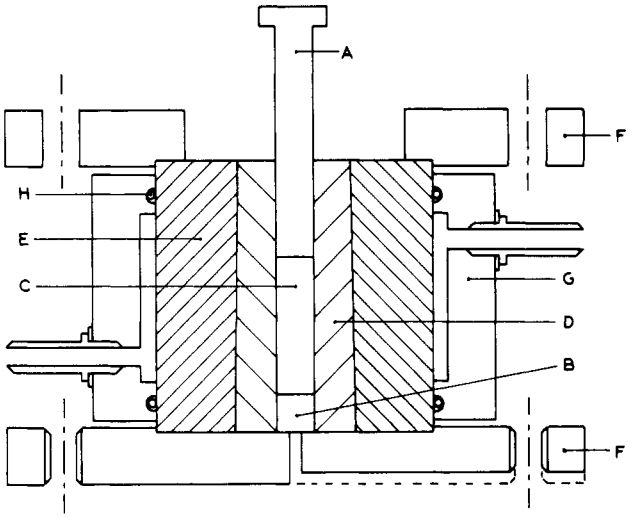
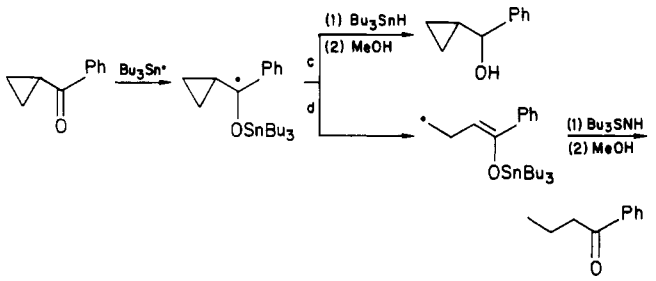


Figure 1. High-pressure vessel: (A) mobile piston; (B) steel stopper; (C) working volume; (D) steel core; (E) steel binding ring; (F) upper and lower plates; (G) heating or cooling jacket; (H) O-ring.

Scheme IV



conclusion is also valid for experiment 11.

Reduction of α,β-Epoxy Ketones. Comparative reductions of α,β-epoxy ketones by tributyltin hydride have also been achieved, and the results are gathered in Table IV. For this type of bifunctional substrates also, we observed a strong influence of the pressure. Whereas reactions performed with a free radical initiator led to the opening of the epoxy ring, the high pressure induces the selective reduction of the carbonyl group. Moreover, the yields are usually very high. These results can be rationalized in the same terms as for the reduction of cyclopropyl ketones.

Conclusion

The high-pressure technique has been shown to be valuable for the reduction of ketones by tributyltin hydride. No radical initiator or Lewis acid catalysts were necessary. Sterically hindered ketones were reduced in good yields and cyclopropylic and epoxidic ketones led in very high yield to alcohols with a predominant or total preservation of the three-membered ring.

Experimental Section

^{1}H NMR spectra were recorded on a Perkin-Elmer R-12 spectrometer. Gas chromatographic analyses were performed on an Intersmat IGC 120FB apparatus equipped with an ionization flame detector. The high-pressure equipment currently used is a piston–cylinder vessel (Figure 1). It is suitable for pressures up to 1500 MPa. The temperature can be adjusted from −20 to 130 °C by appropriate fluid circulation in the external jacket. Chemicals are pressurized in a Teflon cell (Figure 2a) fitting precisely in the inner core of the vessel, the reaction volume being ca. 2 mL. The mobile piston is forced into the vessel by a 30-ton ram. No transmitting fluid is used. The applied force is measured by a captor which indications are regularly correlated to the inner pressure with a manganin gauge (Figure 2b).

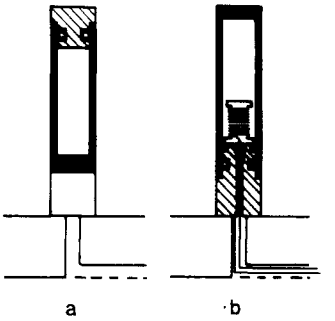


Figure 2. Teflon cell (a) and manganin gauge (b).

Reduction of Sterically Hindered Ketones. Tributyltin hydride was prepared by an exchange reaction between hexabutylditin oxide and a SiH containing polysiloxane.[11] 3,5,5-Trimethylcyclohexanone was prepared by free radical addition of tributyltin hydride on 3,5,5-trimethyl-2-cyclohexenone and subsequent hydrolysis.[12] Ketones used in experiments 2 and 5 were purchased from Aldrich. Other ketones were prepared by the addition of the appropriate Grignard reagent on hydratropic aldehyde (experiments 4, 6, and 7) or on benzaldehyde (experiment 3), followed by oxidation.[2] A typical procedure for the reduction was the following: the ketone (0.015 mol) and tributyltin hydride (0.015 mol) were mixed in 5 mL of dry methanol, and the solution was divided in two parts. One part was pressurized at room temperature under 1000 MPa and then heated at 55 °C for 24 h. The second part was heated at 55 °C under atmospheric pressure for 24 h. The reaction products were identified by comparison with samples obtained by reduction of the ketones with $LiAlH_4$. Alcohols obtained from experiments 2 and 5 were also available from Fluka. Other alcohols were described in ref 3 (experiment 1), 2 (experiment 3), and 2a (experiments 4, 6, and 7). GC analyses were performed with a $^1/_8$ in. × 10 ft column packed with 10% UCON 50HB 2000 on chromosorb W 80–100. In experiments 4, 6, and 7, threo and erythro isomers were identified by their retention time.[10b] In experiment 1, the diastereoisomers were identified following ref 4.

Reduction of Cyclopropyl Ketones. Methyl cyclopropyl ketone and phenyl cyclopropyl ketone were purchased from Fluka. The ketone used for experiment 10 was prepared by a Simmons–Smith reaction on the (*E*)-2-methyl-4-hexen-3-ol[7,13,14] followed by an oxidation step. The same procedure was used for the bicyclo[4.1.0]-2-heptanone (experiment 11).[14] A typical procedure for the stannane reduction was as follows: a mixture of ketone and tributyltin hydride (in 10% excess) was divided into three parts. One part was pressurized as previously at 55 °C for 24 h. The second part was heated for 24 h at 55 °C under atmospheric pressure. The third part was heated at 55 °C for 24 h in the presence of AIBN. The reaction mixture was then poured into a large excess of methanol. GC analyses were performed on a $^1/_8$ in. × 6 ft column packed with 10% Carbowax 20M on Chromosorb W AW DMCS 80-100 by comparison with authentic samples. Alcohols and ketones obtained in experiments 8 and 9 were available from Fluka. Products from experiment 10 were prepared independently following ref 7 and 13. Alcohol obtained in experiment 11 was also prepared following ref 14, and 3-methylcyclohexanone and cycloheptanone were available from Fluka.

Reduction of α,β-Epoxy Ketones. The epoxy ketones used in experiments 12–14 were prepared following ref 15. The experimental procedure was identical with that for the reduction of cyclopropyl ketones. For experiments 13 and 14, a phase separation occurred during the pressurization, and very poor yields were obtained. The difficulty was overcome by adding anhydrous ether until the concentration was ca. 2 M. After methanolysis,

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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.

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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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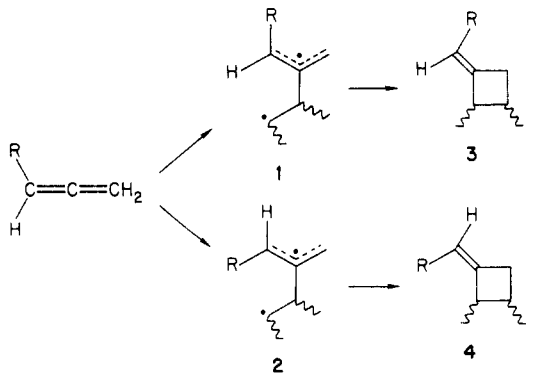
Phenylallene (PHA) reacts with 1,1-dichloro-2,2-difluoroethene (1122) to produce, in part, the two benzylidene-containing cycloadducts **5** and **6**, with the *E* isomer **5** predominating as expected. In addition, two stereoisomeric 2:1 PHA–1122 adducts of structure **8** and **9** are formed by 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.

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