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DIRECT CONVERSION OF ALKENES INTO METHYL-SUBSTITUTED CYCLOPROPANES USING AN ORGANOIRON ETHYLIDENE TRANSFER REAGENT *

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Summary

$(\eta^5\text{-}C_5H_5)(CO)_2FeCH(CH_3)SPh$ (**8**) serves as a quite useful reagent for the transfer of ethylidene groups to alkenes to give methyl-substituted cyclopropanes in good yields. The reaction is accomplished by allowing **8** to react with an alkylating agent such as trimethyloxonium tetrafluoroborate or methyl fluorosulfonate in the presence of the alkene substrate. The active ethylidene transfer reagent is apparently a sulfonium salt which is too reactive to be isolated under normal conditions. In all cases, cyclopropanes are obtained stereospecifically with respect to the configuration of the starting alkenes, and with certain classes of substrates such as *cis*-disubstituted alkenes, the reaction also occurs with very high *syn*-stereoselectivity.

Introduction

Cyclopropanes are most commonly prepared through use of various reagents that effect the addition of methylene or, to be more general, alkylidene groups to the carbon–carbon double bond of alkenes [3]. Among the species that are most frequently employed are carbenes (or carbenoids) and diazo compounds. With the discovery of carbene complexes (**1**) of transition metals through the pioneering efforts of Fischer a number of years ago, the possibility arose of using these compounds as cyclopropanation reagents [4,5]. To date the most useful complexes in this regard have been those of the cyclopentadienyldicarbonyliron system (**2**). The key finding in this area was the observation by Pettit in 1966 that the treatment of the ether derivative **3** with acid in the presence of alkenes leads to the production of

* Taken in part from the Ph.D. dissertation of K.A.M.K. [1a], for a preliminary account see ref. 1b; presented in part at the 181st meeting of the American Chemical Society, Atlanta, GA [2].

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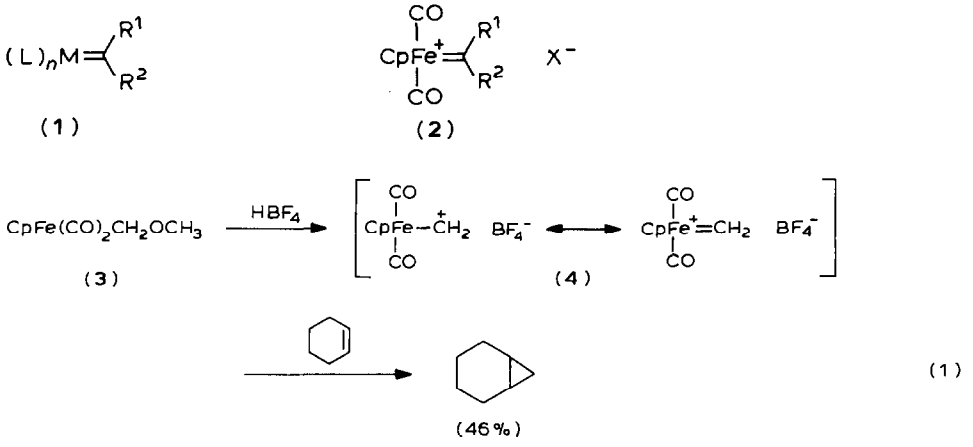
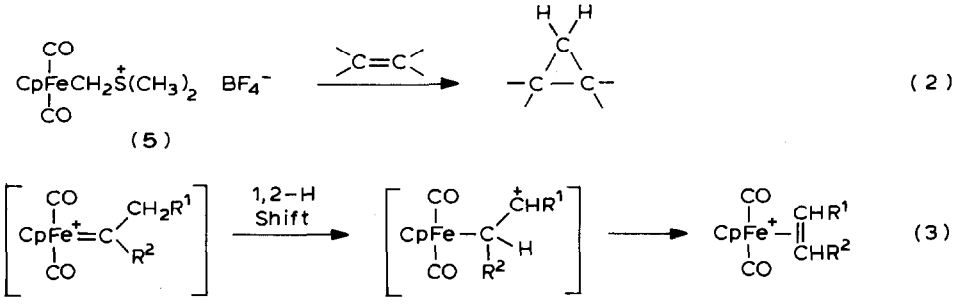
cyclopropanes, apparently via formation and subsequent reaction of the very reactive and unstable cationic methylene complex **4** (eq. 1) [6]; very similar results were also reported by Green shortly afterwards [7]. Since these early studies, a number of other investigations of related iron carbene complexes have been pursued [8]. Particularly noteworthy has been the work of Brookhart [9].



(1)

Our laboratory has been focusing attention primarily upon developing practical, synthetically useful organoiron reagents for the direct cyclopropanation of alkenes [1b,10]. The first reagent **5** which we studied permits the high-yield transfer of the simple methylene group to alkenes (eq. 2) [10a,b]. Whether this type of reagent could be modified to permit the transfer of more complex alkylidene groups was at issue because of the possibility of 1,2-hydrogen shifts occurring within the intermediate alkylidene complexes (eq. 3) [8g,10c,11] in competition with the desired cyclopropanations.

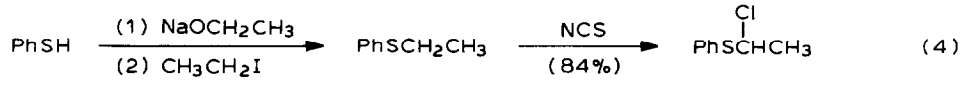


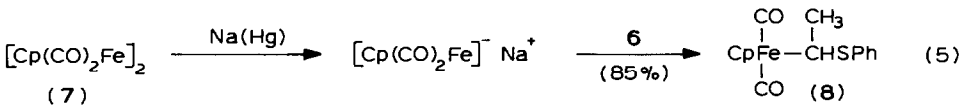
To be noted is that for the well-known Simmons–Smith cyclopropanation reaction [3b], there have been only a limited number of reports of transferring other than methylene groups, and in these cases, the yields are frequently low [12]. We, however, have been able to develop an efficient ethylidene transfer reagent for which we presently wish to report the details of our studies [1].

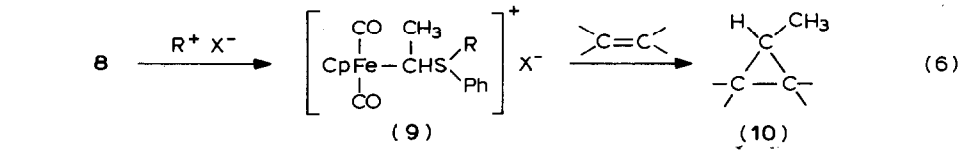
Results and discussion

The preparation of the ethylidene transfer reagent is based upon the procedure which we developed for the simpler reagent **5** [10a,b]. Required as a starting material

is 1-chloroethyl phenyl sulfide (**6**) which is prepared by alkylation of benzenethiol with ethyl iodide followed by chlorination with *N*-chlorosuccinimide (eq. 4) [13]. Reaction of this sulfide with sodium cyclopentadienyldicarbonylferrate, itself obtained in the usual manner by reductive cleavage of the commercially available or easily prepared dinuclear complex **7** [14], results in alkylation at iron [15] to give the desired reagent **8** which is purified according to the modified flash chromatography procedure which we have recently developed [16]. This sulfide derivative is obtained as a yellow, crystalline solid which is reasonably stable to air in that its routine handling (e.g. weighing and transferring) requires no special precautions, although for long-term storage we recommend that it be kept under an inert atmosphere in a freezer. We have been able to store samples in this manner for at least a few years.







The sulfide **8** reacts with various alkylating agents (vide infra) apparently to give sulfonium salts **9** which in turn undergo reaction with alkenes to produce cyclopropanes **10** (eq. 6). However, unlike the case of our methylene transfer reagent **5**, the salts **9** are apparently of limited stability in that we have not been able to isolate and characterize them. Therefore, for purposes of developing a practical synthetic reagent, we chose to employ the neutral sulfide **8** as a compound which may be stored for long periods and then used to generate the requisite sulfonium salts in situ whenever a cyclopropanation is to be performed. Before presenting our cyclopropanation results in detail, though, we will first discuss the optimization of several parameters for these reactions.

The initial optimization studies were done with methyl fluorosulfonate (Magic Methyl; Caution: this very volatile and highly toxic compound must be handled with extreme care [17]) as the alkylating agent, *cis*-cyclooctene as the alkene substrate, and methylene chloride as the solvent. As shown by the temperature studies in Table 1, the optimum temperature for the cyclopropanation reaction is approximately 25°C. A side product, 3-ethylcyclooctene, which is formed in varying amounts under various conditions, is the major product at 45°C; a possible pathway for its formation is rearrangement of the normal cyclopropane product. Our results also show that the active ethylidene transfer reagent, most likely **9**, is apparently stable in solution at low temperature but not at room temperature and above. At −80°C or −40°C, a yellow solid is formed upon adding the methyl fluorosulfonate to the solution of the sulfide **8**. The solid does not react with the alkene to produce the cyclopropane if the temperature is maintained at or below −40°C, even after 24 h. However, when the reaction mixture is warmed to room temperature, the cyclopro-

pane is produced over a period of hours. If the methyl fluorosulfonate is added at 0°C, the solid is formed as well but disappears within a few hours as the cyclopropane is formed. The yellow solid is not observed when the methyl fluorosulfonate is added at 25°C or 45°C. That the solid is a sulfonium salt **9** is only an assumption at this point since we have not actually been able to isolate and characterize this expected intermediate.

With a molar ratio of 1/1/1.25 of the sulfide **8**, cyclooctene, and methyl fluorosulfonate, a 1 *M* concentration of **8** in methylene chloride gives a satisfactory yield of the cyclopropane whereas at a concentration of 0.3 *M*, the yield is significantly lower (Table 1). The reaction also proceeds in other solvents such as tetrahydrofuran and *p*-dioxane, but the yields are somewhat reduced compared to the use of methylene chloride. Although the solid sulfide reagent **8** is reasonably stable to air (vide supra), the maintenance of an inert atmosphere during the cyclopropanation reactions is critically important. When the reactions are done in flasks open to the air, no cyclopropane products are detected.

As a result of testing various alkylating agents with *cis*-5-decene as the alkene substrate, trimethyloxonium tetrafluoroborate was found to be the most effective for inducing cyclopropane formation (Table 2). Its use results in approximately 20% improvements in the yields that we had originally reported [1b] for the use of methyl fluorosulfonate. A drawback to using the oxonium salt is that it is somewhat inconvenient to prepare [18] but, on the other hand, it is commercially available, and it is vastly safer to handle than the fluorosulfonate [17]. The triethyloxonium salt, however, gives lower yields than the trimethyl derivative.

The nature of the counterion in the intermediate sulfonium salt is another important factor. On the basis of earlier work with the methylene transfer reagent **5**, we realized the need for either weakly nucleophilic or non-nucleophilic counterions which would not interfere with the subsequent reactions of the iron reagent with alkenes [10a,b]. Indeed, when methyl iodide is used with **8**, only trace amounts of cyclopropanes are detected.

TABLE 1

INVESTIGATION OF TEMPERATURE AND CONCENTRATION EFFECTS

Sulfide **8**		Conversion of cyclooctene (%) [a]	Corrected yield of **A** [b] (%) [c]	Corrected yield of **B** [b] (%) [c]
Concentration (*M*)	Temperature (°C)			
1	−80 → 25	73.7	30.5	19.1
1	−40 → 25	62.3	2.6	42.9
1	0 → 25	75.0 [d]	16.0 [d]	47.0 [d]
1	25	84.6	5.0	65.9
1	45	76.3	31.2	18.5
0.3	25	84.5	8.3	53.6
2 (THF) [e]	0 → 25	43.0 [d]	2.0 [d]	52.0 [d]
2 (*p*-dioxane) [f]	0 → 25	47.0 [d]	2.0 [d]	51.0 [d]

[a] These values indicate the total amount of alkene consumed in each experiment and are obtained by subtracting the amount of unreacted alkene (GLPC determination) from the starting quantity of alkene. [b] **A** = 3-ethylcyclooctene. **B** = *endo*-9-methylbicyclo[6.1.0]nonane. [c] The yields were determined by GLPC using an internal standard and a sample of pure product for calibration. The yields are corrected for the amount of unreacted alkene. [d] These values were estimated from GLPC recorder tracings. [e] THF was employed as solvent instead of CH_2Cl_2. [f] *p*-Dioxane was employed as solvent instead of CH_2Cl_2.

TABLE 2

INVESTIGATION OF ALKYLATING AGENTS

Entry	Alkylating agent [a]	Conversion of *cis*-5-decene (%) [b]	Corrected yield of cyclopropane [c] (%) [b]	Uncorrected yield of cyclopropane [c] (%) [d]
1	$Me_3O^+ BF_4^-$	65	66	43
2	$Me_3O^+ BF_4^-$	75 (2 eq.) [e]	67	50
3	$Me_3O^+ BF_4^-$	– (air) [f]	0	0
4	FSO_3CH_3	62	44	27
5	$Et_3O^+ BF_4^-$	50	50	25
6	MeI	–	< 2	< 2
7	$Me_3O^+ SbCl_6^-$	–	0	0

[a] Except where otherwise noted, 1-equiv. portions of **8** were employed. *cis*-5-Decene was the alkene substrate in each case. [b] These values were determined as described in Table 1 (notes *a* and *c*). [c] The only cyclopropane product detected was all-*syn*-1,2-di-n-butyl-3-methylcyclopropane. [d] These values indicate the actual amount of cyclopropane produced and are not corrected for the amount of unreacted alkene. [e] 2-Equiv. portion of **8** and alkylating agent were employed in this case. [f] The reaction was conducted in the presence of air instead of under a nitrogen atmosphere.

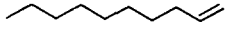
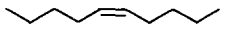
For purposes of performing the above study of parameter effects, only one-equivalent portions of the reagent **8** were employed in the cyclopropanation reactions. As would be expected on the basis of our work with the methylene transfer reagent **5** [10a], the use of excess **8** gives higher yields of final product (Table 2, entry 2). However, in order to give a clearer indication of the actual efficiency of our reactions, we have continued to use only one equivalent of **8** in most of our further studies.

A final parameter which we have investigated is the use of a co-reagent in attempts to promote the loss of the organic sulfide from the intermediate sulfonium salts. However, no significant effects on yields are seen. Results with boron trifluoride etherate as a prospective promoter are summarized in Table 3.

Based upon all of the above results, we have chosen standard conditions for performing cyclopropanations of several representative alkenes (Table 4). The reactions are done at 25°C with methylene chloride as the solvent and in several cases with both methyl fluorosulfonate and trimethyloxonium tetrafluoroborate as alkylating agents in separate runs. We emphasize that these results are obtained using only one equivalent of our reagent **8**. The yields are from GLPC analysis with pure

TABLE 3

EFFECT OF ADDITION OF $BF_3 \cdot Et_2O$

Alkene	Equiv. of $BF_3 \cdot Et_2O$	Conversion of olefin (%) [a]	Corrected yield (%) [a]
	0.0	55.4	70.1 (1/1 *cis*/*trans*)
	0.5	59.4	43.0 (1/1 *cis*/*trans*)
	0.0	62.5	44.4 (*cis*)
	0.5	56.1	49.6 (*cis*)

[a] These values were determined as described in Table 1 (notes *a* and *c*).

TABLE 4

ETHYLIDENE TRANSFER TO OLEFINS WITH $Cp(CO)_2FeCH(CH_3)SPh$ (8)

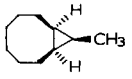
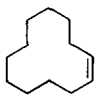
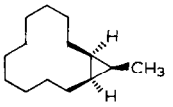
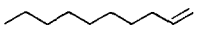
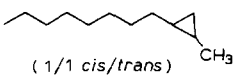
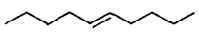
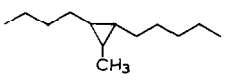
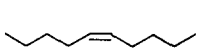
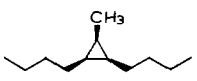
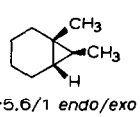
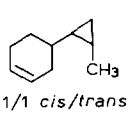
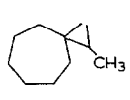
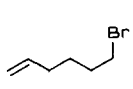
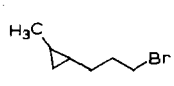
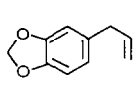
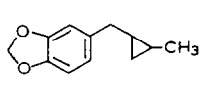
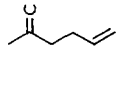
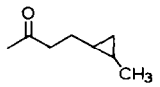
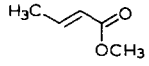
Entry	Olefin	Cyclopropane	Conversion of olefin (%) [a]		Uncorrected yield (%) [a]		Corrected yield (%) [a]	
			MM [b]	TMO [c]	MM [b]	TMO [c]	MM [b]	TMO [c]
1			85	100	60	73	70 [d,e]	73
2			49		34		70 [h]	
3		 (1/1 *cis/trans*)	55	54	39	47	70	87
4			–	29	0	14	0	48 [e]
5			62	65	27	43	44	66 [e]
6			81	100	54	67	67 [e,f]	67
7		 (41/17 *Z/E*)	100	100	58	65	58 [g]	65
8			59		48		81	
9		 (>5.6/1 *endo/exo*)		34		22		66
10		 (1/1 *cis/trans*)		50 [i]		40 [i]		80 [i]
11				100				
12		 (0.9/1 *cis/trans*)		59		50		84
13		 (1.3/1 *trans/cis*)		81		37		46

TABLE 4 (continued)

Entry	Olefin	Cyclopropane	Conversion of olefin (%) [a]		Uncorrected yield (%) [a]		Corrected yield (%) [a]	
			MM [b]	TMO [c]	MM [b]	TMO [c]	MM [b]	TMO [c]
14		 (1.7/1 *trans*/*cis*)		77		21		27
15				–		0		0

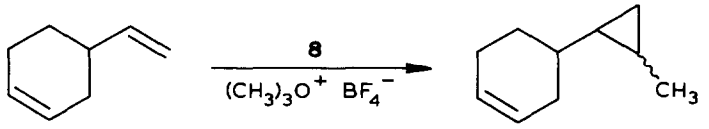
[a] These values were determined as described in Table 1 (notes *a* and *c*) and Table 2 (note *d*). [b] MM: Magic Methyl (methyl fluorosulfonate) was used as the alkylating agent. [c] TMO: trimethyloxonium tetrafluoroborate was used as the alkylating agent. [d] Stereochemistry was determined by ^{1}H NMR as in ref. 12c. [e] This product was the only cyclopropane isomer detected. [f] Stereochemistry was determined by ^{1}H NMR as in ref. 5b and 22; the CH_3 resonance appeared at δ 0.79. [g] The C(2)-CH_3 group appeared in the ^{1}H NMR spectrum at δ 0.76 for the *Z*-isomer and at δ 1.16 for the *E*-isomer. [h] When a mixture of *cis*- and *trans*-cyclododecene is used as in our preliminary communication (see refs. 1b and 20), the expected mixture of cyclopropane products is obtained. [i] These values were estimated from GLPC recorder tracings.

samples of the products having been calibrated against internal standards.

Among the compounds that react satisfactorily with our reagent, those which serve as the best substrates for cyclopropane formation are styrenes and the aliphatic monosubstituted, 1,1-disubstituted, and cyclic and acyclic *cis*-1,2-disubstituted alkenes whereas aliphatic trisubstituted and *trans*-disubstituted alkenes give lower yields. The reaction tolerates various functional groups (halide, ketone, acetal) that are located at sites remote from the alkene double bond. In some cases (e.g. Table 4, entries 1–3), small amounts of olefinic side products are obtained which, like the cyclopropanes, also incorporate an additional C_2H_4 unit relative to the starting alkenes. Steric factors appear to play an important role in the relative reactivities seen above, but electronic effects must also be considered. Consistent with the electrophilic nature that is expected for **8**, cyclopropanations occur well, for the most part, with reasonably electron-rich alkenes but fail for electron-poor substrates such as methyl crotonate. Other compounds which fail to give cyclopropanes include 3-methylcyclohexene, norbornene, phenanthrene, 3-bromocyclohexene, 4-(2′-hydroxyethyl)cyclohexene, 4-penten-1-ol, allyl phenyl sulfide, and 1-methoxycyclooctene. Among the trends seen for these cases are the poor reactivity of most cyclohexene-containing systems toward **8** and the failure of cyclopropanation for compounds containing a reactive functional group on or near the double bond. Perhaps somewhat surprising at first is the negative result obtained for the vinyl ether, 1-methoxycyclooctene, in which the double bond is very electron-rich. A possible explanation is that the desired reaction does indeed occur, but the reactive methoxycyclopropane [3f] that results undergoes further rapid transformations under the reaction conditions.

Of potential use is the dependence of relative reactivities of alkenes upon the nature of the alkylating agent. When methyl fluorosulfonate is employed, *trans*-disubstituted alkenes do not undergo cyclopropanation whereas the reactions succeed at least to a limited extent when the oxonium salt is used. Another case of double

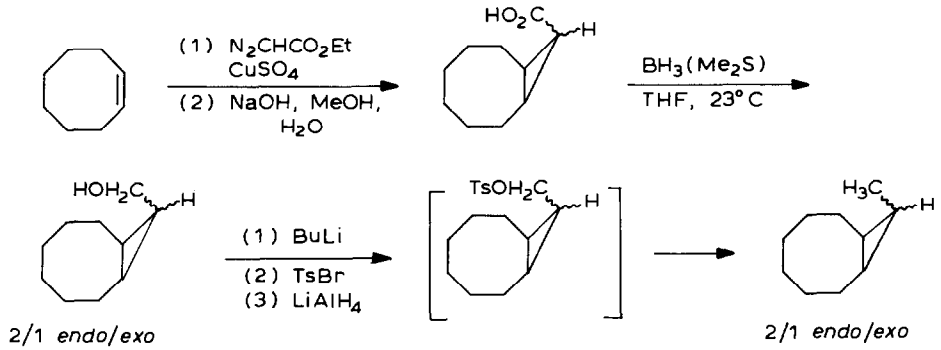
bond selectivity is seen for 4-vinylcyclohexene in which only the monosubstituted alkene undergoes cyclopropanation (eq. 7). In contrast to this result, the Simmons–Smith reaction occurs with both double bonds of this substrate [19]. In fact, there is little similarity between the overall relative reactivities of alkenes in our reaction and in the Simmons–Smith reaction [3b], and therefore the two methods provide good complementary means for accomplishing cyclopropanations.



(7)

As is true of alkylidene transfer reactions of alkenes in general, there are two aspects of the stereochemistry of our reactions that we need to address. First of all, the reactions of **8** proceed with complete stereospecificity with respect to the configurations of the alkene substrates, i.e. within the limits of detection of our instrumentation, we are able to observe only those cyclopropane products in which the original double bond geometry is retained (Table 4, entries 2, 4, and 5), a point which is likely to rule out any simple carbonium ion addition mechanisms for our cyclopropanations. The reactions are also highly stereoselective in many cases with respect to the configuration of the methyl-substituted carbon arising from the reagent **8** relative to the substituents arising from the alkenes. This stereoselectivity is most pronounced for *cis*-1,2-disubstituted alkenes (Table 4, entries 1, 2 [20], and 5), 1-methylcyclohexene (entry 9), and for styrene (entry 6), but is also seen to a lesser extent with some but not all monosubstituted (entries 13 and 14) and 1,1-disubstituted (entry 7) alkenes. The predominant product in these cases is the *endo*-methyl-(or *syn*)-cyclopropane, the more stereochemically encumbered isomer. This phenomenon has been seen for some other cases of alkylidene transfer reactions as well [5b,9a,21,22].

The stereochemistry of our products was deduced primarily from their ^1H and ^{13}C NMR spectra [5b,9a,22]. The *endo*-selectivity was established most conclusively in the case of *cis*-cyclooctene for which a comparison sample of the product was obtained by means of an alternative route (Scheme 1) [23]. The NMR spectrum exhibits an upfield shift for the methyl protons as expected for the *endo* isomer and is consistent with the data of Kawabata [12c].



SCHEME 1

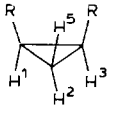
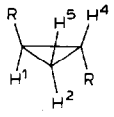
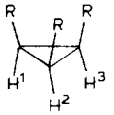
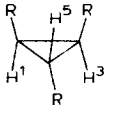
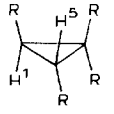
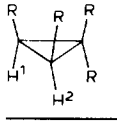
Additionally, a general observation is that cyclopropyl protons positioned *cis* to alkyl groups lie within the shielding region of the ring-to-substituent carbon–carbon

σ-bond and thus exhibit upfield shifts in comparison with cyclopropyl protons oriented *trans* to alkyl groups [22]. Thus, for the *endo* isomer above, the cyclopropyl protons, all of which are *trans* to alkyl residues, appear further downfield than the cyclopropyl protons of, for example, *trans*-1-methyl-2-octylcyclopropane, all of which are *cis* to at least one alkyl group. A summary of our ^{1}H NMR chemical shift data for the cyclopropyl protons of di-, tri-, and tetra-substituted cyclopropanes is given in Table 5.

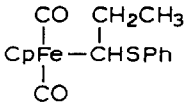
Up to this point, the problem of 1,2-hydrogen shift (eq. 3) which we had anticipated as a possible difficulty in our reactions had not been observed. Therefore, we chose to explore the possibility of extending our present methodology to the transfer of other alkylidene groups. For example, the prospective n-propylidene transfer reagent **10** may be prepared by a route analogous to that used for **8**. When **10** is allowed to react with alkenes under the same alkylation conditions as optimized for **8**, a yellow solid is formed, but it persists even after 40 h at 25°C, and no cyclopropanes are produced. Under more forcing conditions, methylene chloride is

TABLE 5

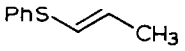
^{1}H NMR CHEMICAL SHIFTS OF CYCLOPROPYL PROTONS

Cyclopropanes (R = alkyl)	δ (ppm)	
1,2-Disubstituted:		
	H(1)–H(3) 0.4 to 0.8	H(5) −0.2 to −0.4
	H(1), H(2), H(4), H(5) 0.0 to 0.4	
1,2,3-Trisubstituted:		
	H(1)–H(3) 0.4 to 0.8	
	H(1), H(3) 0.30 to 0.65	H(5) −0.1 to 0.25
1,1,2,3-Tetrasubstituted:		
	H(1), H(5) −0.2 to −0.3	
	H(1), H(2) 0.1 to 0.6	

replaced as the solvent by *p*-dioxane, and the reaction mixture is heated at up to 60°C until the yellow solid decomposes. Still no cyclopropanes are produced, but rather the propenyl sulfide **11** is obtained, thus indicating that a type of β-hydrogen reactivity may be operative in these systems after all. To circumvent this problem, we have successfully developed alternative approaches for the transfer of various complex alkylidene group as reported elsewhere [10c,d].

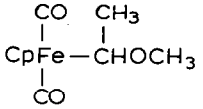


(10)



(11)

As mentioned in the introduction, Professor Brookhart's research group has also been very active in this area, and therefore comparison of their results with ours is in order. Most relevant to our present report is their concurrent development of an attractive ether-based ethylidene transfer reagent **12** [9a]. In comparing the relative efficiencies of cyclopropanations using **8** and **12**, one must bear in mind that most of the yields reported for **12** are based upon the use of a two-fold excess of this reagent or of the alkene as opposed to the use of 1/1 stoichiometry under our standard conditions. In the few directly comparable cases in which **12** has been used in a 1/1 stoichiometry, our yields using **8** are very much higher, and even in some of the cases in which excess **12** has been used, our yields remain higher despite the fact that we have used only equimolar proportions. Another factor to be noted once again is the rather stable, crystalline nature of our reagent, whereas the characteristics of **12** are not apparent from the published data [9a]. Points of similarity between our work and that of Brookhart are that *endo*-selectivity is seen for both **8** and **12** and that his group's attempts to perform propylidene transfer reactions were, like ours, unsuccessful.



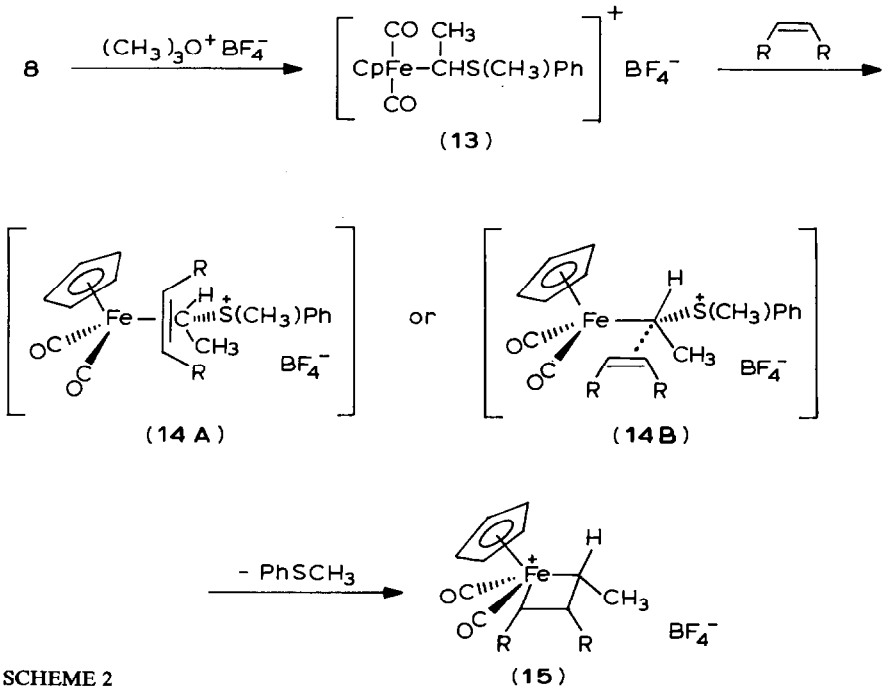
(12)

With respect to the mechanism of our cyclopropanation reaction, if we were to invoke the intermediacy of an ethylidene complex of iron (**2**, $R^1 = CH_3$, $R^2 = H$), there already exist in the literature some very good explanations which not only indicate how cyclopropanes may be produced by reactions of alkylidene species with alkenes, but they also serve to explain, at least in part, the *endo*-selectivity of the reactions [4,5b,f,9,22a,24]. Furthermore, various ethylidene (and, for that matter, propylidene) complexes have actually been formed as observable intermediates [9a,25]. Therefore, our further speculation on the possible role of an ethylidene complex in our reactions would serve little purpose at this time.

A more substantive point to raise is whether an ethylidene complex is necessarily formed as a mandatory intermediate in our reactions. We do not intend to exclude the pathways proposed by others [4,5b,f,9,22a,24], but rather, we simply wish to draw attention to an alternative pathway which may be given at least preliminary consideration. Our reasons for considering other possibilities are that first of all, we have no direct evidence for the generation of an ethylidene intermediate, and secondly, the sulfonium salt that is likely to be formed in our reactions should be

less susceptible to dissociation than the much less stable oxonium species involved, for example, in Brookhart's work [9]. Consequently, we should be concerned with the question of how a salt such as **13** (Scheme 2) could be involved in cyclopropane formation without first undergoing conversion to an ethylidene complex. A tentative picture which fits our results reasonably well is depicted in Scheme 2 in which a bimolecular reaction is shown. We have chosen a conformation of the salt in which the methyl substituent on the latent "carbene" center is oriented away from the sterically demanding cyclopentadienyl ring and in which both the departing sulfide and the incoming alkene are able to avoid direct interaction with this ring as well. The alkene may then adopt a range of possible orientations as it approaches the salt. At either end of this range are the orientations indicated by **14A** and **14B** in which the substituents of the alkene are directed away from the cyclopentadienyl group. As the neutral sulfide is lost from the salt, further collapse of the alkene/reagent complex may lead to intermediates similar to those previously proposed for related cyclopropanations. Included as a possibility would be the metallacyclobutane **15**. At what point in this pathway the alkene first interacts with the iron center is open to question. Note that we have shown this pathway for a *cis*-disubstituted alkene in order to account for the high stereoselectivity that is seen when this type of substrate is employed; reductive elimination from **15** would give the *endo*-methylcyclopropane.

Should this picture or a related one be valid, then the lack of 1,2-hydrogen shifts in our ethylidene transfer reactions would certainly be understandable because of the absence of an alkylidene complex as an actual intermediate. However, the reason for failure of our attempted propylidene transfer reactions is not clear from this picture. Another argument against this alternative pathway is the unfavorable steric



SCHEME 2

crowding in **14A** and **14B** which may make the bimolecular mechanism unlikely. On the other hand, in work to be reported elsewhere, we have shown that the related sulfonium salt **5** undergoes facile exchange with various organic sulfides without decomposition via carbene-like pathways. Detailed mechanistic studies are clearly needed to resolve these issues. Without these studies, the bulk of the evidence from the earlier literature tends to support the intermediacy of a carbene complex, but the alternative pathway cannot be ruled out entirely yet [25A].

Conclusion

This work has resulted in the development of a practical, synthetically useful reagent for the direct conversion of alkenes into methyl-substituted cyclopropanes by means of ethylidene transfer. Our methodology should be applicable to various natural products containing three-membered rings with this substitution pattern [26]. Alternative approaches which we have reported elsewhere are complementary to the present work in permitting the construction of a variety of other cyclopropane systems [10].

Experimental section

A. General

All reactions involving air-sensitive compounds were performed under a nitrogen atmosphere using double manifold techniques. Solutions were transferred with either double-ended needles or hypodermic syringes.

The air-free, anhydrous solvents employed in these reactions were freshly distilled under nitrogen from dark blue or purple solutions of sodium benzophenone anion or dianion in the case of tetrahydrofuran, diethyl ether, *p*-dioxane, pentane, and benzene, or from P_2O_5 in the case of methylene chloride. Most commercially obtained reagents were distilled or recrystallized and stored under nitrogen prior to use. Organolithium reagents were stored and manipulated under nitrogen and titrated prior to use.

B. Apparatus

A Neslab Cryo-Cool Model CC-100 F with an acetone bath was employed for low temperature reactions of long duration. For short durations either dry ice-acetone ($-78°C$), dry ice/carbon tetrachloride, or ice/water baths were used.

^1H NMR spectra were recorded with Varian EM-360, Varian HFT-80, or Nicolet NT-300 spectrometers. ^{13}C NMR spectra were recorded on either Varian CFT-20 or Nicolet NT-300 spectrometers. Carbon multiplicities were determined by either off-resonance decoupling techniques or by the attached proton test [27]. The IR spectra were obtained with a Pye–Unicam Model SP-1000 spectrometer as KBr wafers and were calibrated with a polystyrene standard. Mass spectra were recorded with Hewlett–Packard Model 5982A and AEI Model MS-30 mass spectrometers by using electron impact ionization at 70 eV. Elemental analyses were performed by Galbraith Laboratories, Inc. The analytical results are given only when they agree with the calculated values within $\pm 0.3\%$. In all other cases, the homogeneity of the compounds was demonstrated by careful GLPC and molecular formulas were determined by high resolution mass spectroscopy.

Preparative GLPC was performed with a Varian Aerograph Model 900 gas chromatograph using a 6-ft × 1/2-in 5% SE-30 column. Analytical GLPC was performed with a Hewlett–Packard Model 5911 or a Varian Aerograph Series 1400 chromatograph equipped with a flame ionization detector, a linear temperature programmer, and a Hewlett–Packard 3380 A electronic integrator. A 6-ft × 1/8-in 5% OV-1 column was used. Separations involving the use of medium pressure liquid chromatography were performed by the modified "flash" chromatography technique developed in these laboratories [16] for use with air-sensitive compounds. Crude products were generally purified by bulb-to-bulb distillation at reduced pressure.

C. Procedures

Ethyl phenyl sulfide. A procedure similar to Otto's was followed [28]. Into a 2 l flask was added sodium (11.5 g, 0.5 mol) and absolute ethanol (1 l). The flask was placed under nitrogen, cooled to 0°C, and stirred until all the sodium dissolved. Thiophenol (51.3 ml, 0.5 mol) was then added over a period of several minutes, and the mixture was allowed to reach room temperature. After 1 h, the mixture was again cooled to 0°C in an ice bath and ethyl iodide (39.9 ml, 0.5 mol) was added dropwise over a period of several minutes. The ice bath gradually warmed to room temperature. After 17 h the reaction mixture was concentrated in vacuo or by distilling off the ethanol. The residue was partitioned between 10% aq. sodium hydroxide (250 ml) and diethyl ether (250 ml). The organic layer was washed with water (3 × 250 ml) and sat. aq. sodium chloride (250 ml), dried over anhydrous magnesium sulfate, and concentrated in vacuo leaving 62.8 g of a clear orange solution. Distillation under reduced pressure afforded 52.9 g (77%) of a clear, colorless liquid: b.p. 49°C (0.12 torr; lit. [28] b.p. 84°C, 10 torr); ^{1}H NMR ($CDCl_3$) δ 7.1–7.5 (m, 5 H, Ar*H*), 2.88 (q, *J* 7 Hz, 2 H, CH_2), 1.27 (t, *J* 7 Hz, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 136.75 (C_{ipso}), 129.14, 128.86 (C_{meta}, C_{ortho}), 125.81 (C_{para}), 27.72 (CH_2), 14.41 (CH_3).

α-Chloroethyl phenyl sulfide (6). The procedure of Tuleen and Stephens was employed [13] To a solution of ethyl phenyl sulfide (5.2 g, 37.7 mmol) and carbon tetrachloride (52 ml) at 0°C in a 250-ml flask was added solid *N*-chlorosuccinimide (5.03 g, 37.7 mmol). The mixture was then placed under a nitrogen atmosphere, stirred, and allowed to reach room temperature gradually. After a total of 17 h, the light yellow mixture was filtered to remove white solid, and the filtrate was concentrated in vacuo. The residual light-yellow colored liquid was distilled under reduced pressure to afford 5.44 g (84%) of the chloro sulfide as a clear colorless liquid: b.p. 43–47°C (0.05 torr; lit. [13] b.p. 75–78°C, 0.4 torr); ^{1}H NMR ($CDCl_3$) [13] δ 7.2–7.7 (m, 5 H, Ar*H*), 5.45 (q, *J* 7 Hz, 1 H, C*H*CH_3), 1.8 (d, *J* 7 Hz, 3 H, CHCH_3).

η^5-Cyclopentadienylbis(carbonyl)(1-phenylthioethyl)iron(II) (8). To a 500-ml flask with a side arm was added 1% sodium amalgam (83.2 g) and $[CpFe(CO)_2]_2$ (5.12 g, 14.5 mmol). The flask was placed under nitrogen, and air-free, anhydrous tetrahydrofuran (73 ml) was added [14]. After stirring for 1 h at 25°C, the mixture was cooled to 0°C and α-chloroethyl phenyl sulfide (5.0 g, 29.0 mmol) was added dropwise. The mixture was allowed to warm gradually to room temperature, and after a total of 17 h, the reaction was terminated by addition of air-free anhydrous methylene chloride (120 ml) via double-ended needle. After allowing the precipitated salts to settle for several hours, the organic layer was transferred with a double-ended

needle to a Schlenk filter tube under nitrogen and filtered through diatomaceous earth topped by sea sand into a three-neck 250-ml flask. The filtrate was evaporated into a liquid nitrogen cooled 1-l flask, leaving a dark brown residue. The NMR sample was prepared under nitrogen and filtered through a Schlenk filter tube: ^{1}H NMR ($CDCl_3$) δ 7.1–7.7 (m, 5 H), 5.0 (s, 5 H), 3.7 (q, J 7 Hz, 1 H), 1.5 (d, J 7 Hz, 3 H). The crude product was conveniently purified through use of our modified "flash" chromatography procedure [16].

Degassed solvents (1.5/1 hexanes/methylene chloride) were used, and the entire procedure was performed under a nitrogen atmosphere. After the column was prepared according to our procedure [16], the crude product was dissolved in methylene chloride, and was applied to a 60-mm diameter column with a syringe through a septum placed over an auxiliary port of the redesigned flow controller. The column was eluted at a rate of 0.5 in/min, and two fractions were collected. The first consists of a yellow band, not completely separated from the second which consists of an orange band. Both fractions were then concentrated under vacuum. Fraction 1 yielded an unidentified oil. Fraction 2 yielded pure yellow crystals (m.p. 59°C). (The column was then flushed with pure methylene chloride, and the separation procedure was repeated for the remaining half of the crude product.) Altogether, 7.75 g (85.4%) of **8** was obtained as yellow crystals: ^{1}H NMR ($CDCl_3$) δ 7.1–7.5 (m, 5 H, ArH), 4.93 (s, 5 H, C_5H_5), 3.78 (q, J 6.8 Hz, 1 H, CHCH$_3$), 1.58 (d, J 6.8 Hz, 3 H, CHCH_3); ^{13}C NMR ($CDCl_3$) δ 216.09 (CO), 215.74 (CO), 141.32 (C_{ipso}), 129.21, 128.49 (C_{meta}, C_{ortho}), 125.26 (C_{para}), 86.18 (C_5H_5), 55.73 (FeCH), 22.35 (CH$_3$); IR (KBr pellet) 2900 (CHCH$_3$), 1990 (CO), 1930 (CO), 1580 (phenyl), 1475 (phenyl), 1435 (CH$_3$), 1365 (CH$_3$), 835 (Cp), 630 (Cp).

η^5-Cyclopentadienylbis(carbonyl)iron dimer (7). The preparation follows the procedure of King [29]. (Caution: To prevent decomposition, the reaction mixture should not be heated above 140°C.) This resulted in 44.1 g (91.3%) of red-brown crystals: IR (KBr pellet) [29] 1970 (C=O), 830 (aromatic), 670 (aromatic).

Ethylidenation of olefins with methyl fluorosulfonate. General procedure. Into a 10 ml flask was placed the sulfide complex **8**. The flask was then equipped with a condenser to minimize evaporation of volatile hydrocarbons, placed under nitrogen, and charged with air-free, anhydrous methylene chloride (1 M), the olefin (1 equiv.) and methylfluorosulfonate (1.25 equiv.). After being stirred at 25°C for 12–20 h, the reaction mixture was diluted with pentane to precipitate the iron-containing byproducts, washed with water and saturated sodium chloride, dried over magnesium chloride and concentrated in vacuo. The residue was purified on a silica gel column, concentrated in vacuo and bulb-to-bulb distilled. Preparative GLPC was performed to isolate the pure cyclopropanes using a 6-ft × 1/2-in 5% SE-30 column. The yields of the products and the amounts of the unreacted olefins were determined by analytical GLPC of the crude reaction mixture using a 6-ft × 1/8-in 5% OV-1 column after calibration of the instrumentation with pure samples of the products and starting olefins and through use of internal standards (straight chain hydrocarbons).

Ethylidenation of olefins with trimethyloxonium tetrafluoroborate. General procedure. The procedure is the same as with methyl fluorosulfonate except that both solid sulfide **8** and trimethyloxonium tetrafluoroborate (1.25 equiv.) are initially added to the reaction flask, which is then placed under nitrogen and charged with air-free, anhydrous methylene chloride and the olefin.

Characterization of methylcyclopropane products

From cyclooctene

endo-9-Methylbicyclo[6.1.0]nonane. ^{1}H NMR ($CDCl_3$) [12c] δ 1.1–1.6 (m, 12 H, CH_2's), 0.90 (d, J 4 Hz, 3 H, CH_3), 0.4–0.8 (m, 3 H, H(1), H(8), H(9)); ^{13}C NMR ($CDCl_3$, off-resonance), 29.80 (t, CH_2), 26.77 (t, CH_2), 21.55 (t, CH_2), 17.90 (d, CH), 11.33 (d, CH), 7.83 (q, $CHCH_3$).

3-Ethylcyclooctene. ^{1}H NMR ($CDCl_3$) δ 5.63 (m, 2 H, CH=CH), 2.0–2.3 (m, 3 H, CHCH=CH), 1.0–1.7 (m, 12 H, CH_2's), 0.89 (t, 3 H, CH_3).

From cis-cyclododecene

syn-1,12-endo-13-Methylbicyclo[10.1.0]tridecane. ^{1}H NMR ($CDCl_3$) δ 0.95–1.8 (m, 20 H, CH_2's), 0.83 (d, J 2.4 Hz, CH_3), 0.45–0.75 (m, 3 H, H(1), H(12), H(13)); ^{13}C NMR ($CDCl_3$, APT) δ 28.56 (2 CH_2), 27.10 (2 CH_2), 26.41 (2 CH_2), 23.10 (2 CH_2), 20.25 (2 CH_2), 18.44 (2 CH), 10.94 ($CHCH_3$), 8.08 (CH_3).

From trans-cyclododecene

anti-1,12-13-Methylbicyclo[10.1.0]tridecane. ^{1}H NMR ($CDCl_3$) δ 1.1–2.0 (m, 20 H, CH_2's), 0.98 (d, J 5.7 Hz, 3 H, CH_3), −0.1–0.25 (m, 1 H, $CHCH_3$), 0.3–0.65 (m, 2 H, H(1), H(12)); ^{13}C NMR ($CDCl_3$, APT) δ 33.49 (CH_2), 28.09, 27.86, 27.32, 25.87, (5 CH_2), 25.54 (CH), 25.12, 25.02, 24.38, 23.60 (4 CH_2), 21.76, 17.74 (2 CH), 13.09 (CH_3).

3-Ethylcyclododecene. ^{1}H NMR ($CDCl_3$) δ 5.18 (m, 2 H, CH=CH), 2.1–2.6 (m, 3 H, CHCH=CH), 1.0–2.1 (m, 20 H, CH_2's), 0.90 (t, J 6.4 Hz, 3 H, CH_3).

From 1-decene

cis-1-Methyl-2-octylcyclopropane. ^{1}H NMR ($CDCl_3$) δ 1.1–1.6 (m, 12 H, CH_2's), 1.0 (d, J 5 Hz, 3 H, $CHCH_3$), 0.88 (t, 3 H, CH_2CH_3), 0.5–0.7 (m, 3 H, cyclopropyl H *trans* to alkyl groups), −0.3 to −0.4 (m, 1 H, cyclopropyl H *cis* to alkyl groups); ^{13}C NMR ($CDCl_3$) δ 32.08, 30.31, 29.83, 29.51, 28.62, 22.82, 15.84, 14.18, 13.31, 12.10, 9.44; Anal. Found: C, 85.72; H, 14.17. $C_{12}H_{24}$ calcd.: C, 85.63; H, 14.37%.

trans-1-Methyl-2-octylcyclopropane. ^{1}H NMR ($CDCl_3$) δ 1.1–1.6 (m, 12 H, CH_2's), 0.6–1.0 (overlapping $CHCH_3$ and CH_2CH_3 multiplets, 6 H), 0.0–0.4 (m, 4 H, CH); ^{13}C NMR ($CDCl_3$) δ 34.38, 32.03, 29.77, 29.61, 29.45, 22.78, 20.05, 19.14, 16.20, 14.17, 12.98, 12.75; Anal. Found: C, 85.65; H, 14.19. $C_{12}H_{24}$ calcd.: C, 85.63; H, 14.37%.

From trans-5-decene

trans-1,2-Dibutyl-3-methylcyclopropane. ^{1}H NMR ($CDCl_3$) δ 1.1–1.6 (m, 12 H, CH_2's), 1.01 (d, J 6 Hz, 3 H, $CHCH_3$), 0.9 (m, 6 H, 2 CH_2CH_3), 0.3–0.5 (m, 2 H, H(1), H(2)), 0.0 (m, 1 H, H(3)); ^{13}C NMR ($CDCl_3$, APT) δ 34.17 (CH_2), 32.57 (CH_2), 32.01 (CH_2), 29.03 (CH_2), 26.52 (CH), 23.36 (CH), 22.78 (CH_2), 22.53 (CH_2), 16.96 (CH), 14.21 (2 CH_2CH_3), 13.09 ($CHCH_3$); *m/e* calcd. for $C_{12}H_{24}$ 168.1878 obsd. 168.1926.

From cis-5-decene

cis-1,2-Dibutyl-3-methylcyclopropane. ^{1}H NMR ($CDCl_3$) δ 1.2–1.4 (m, 12 H, CH_2's), 0.90 (m, 9 H, overlapping $CHCH_3$ and CH_2CH_3 multiplets) 0.75 (m, 1 H,

$CHCH_3$), 0.62 (m, 2 H, $CHCH_2$); ^{13}C NMR ($CDCl_3$, APT) δ 32.61 (CH_2), 22.93 (CH_2), 22.87 (CH_2), 17.83 (2 $CHCH_2$), 14.22 (2 CH_2CH_3), 11.20 ($CHCH_3$), 7.65 ($CHCH_3$); Anal. Found: C, 85.59; H, 14.36. $C_{12}H_{24}$ calcd.: C, 85.63; H, 14.37%.

From styrene

cis-1-Methyl-2-phenylcyclopropane. ^1H NMR ($CDCl_3$) spectrum was identical with authentic sample synthesized by Mathias and Weyerstahl [22b]; ^{13}C NMR ($CDCl_3$) δ 129.37 (C_{ipso}), 128.62, 127.92 (C_{meta}, C_{ortho}), 126.66 (C_{para}), 21.20 (CH_2), 13.67 (CH), 12.72 (CH), 10.96 (CH_3).

From α-methylstyrene

E-1,2-Dimethyl-1-phenylcyclopropane. ^1H NMR ($CDCl_3$) δ 7.1–7.3 (m, 5 H, Ar*H*), 1.35 (s, 3 H, $ArCCH_3$), 1.16 (d, *J* 4 Hz, 3 H, $CHCH_3$), 1.06 (m, 2 H, CH_2), 0.3 (m, 1 H, $CHCH_3$).

Z-1,2-Dimethyl-1-phenylcyclopropane. ^1H NMR ($CDCl_3$) δ 7.1–7.3 (m, 5 H, Ar*H*), 1.33 (s, 3 H, $ArCCH_3$), 0.76 (m, 3 H, $CHCH_3$), 0.5–0.7 (m, 3 H, overlapping CH_2 and $CHCH_3$ cyclopropyl proton multiplets).

From diphenylethylene

1,1-Diphenyl-2-methylcyclopropane. ^1H NMR ($CDCl_3$) δ 7.0–7.4 (m, 10 H, Ar*H*), 1.1–1.9 (m, 3 H, overlapping CH_2 and $CHCH_3$ cyclopropyl proton multiplets), 0.92 (d, *J* 6 H, 3 H, $CHCH_3$); *m/e* calcd. for $C_{16}H_{16}$ 208.1286, obsd. 208.1255.

From 1-methyl-1-cyclohexene

exo- and endo-1,7-Dimethylbicyclo[4.1.0]heptane. ^1H NMR ($CDCl_3$) δ 1.0–1.6 (m, 8 H, CH_2's), 1.02 (s, 3 H, CH_3), 0.94 (d, *J* 7 Hz, 3 H, $CHCH_3$), 0.1–0.6 (m, 1 H, C*H* of *endo* overlapping with $CHCH_3$ of *endo*), −0.3 to −0.2 (m, 1 H, $CHCH_3$ of *exo* overlapping with C*H* of *exo*); *m/e* calcd. for C_9H_{16} 124.1252, obsd. 124.1265 (*endo*), 124.1282 (*exo*). *endo/exo* > 5.6/1 (NMR integration).

From 4-vinyl-1-cyclohexen-1-yl

trans-1-Methyl-2-[cyclohex-3-en-1-yl]cyclopropane. ^1H NMR ($CDCl_3$) δ 5.63 (m, 2 H, C*H*=C*H*), 1.8–2.1 (m, 4 H, CH_2=CH_2), 1.2–1.6 (m, 3 H, overlapping multiplets of $CHCH_2CH_2$), 1.01 (d, *J* 5.1 Hz, 3 H, $CHCH_3$), 0.1–0.6 (m, 4 H, overlapping cyclopropyl proton multiplets); ^{13}C NMR ($CDCl_3$, APT) 126.93 (CH=CH), 126.66 (CH=CH), 38.61 ($CH(CH_2)_2$), 31.72 (CH_2), 31.43 (CH_2), 28.45 (CH_2), 25.27 (CH_2), 19.25 (CH), 11.45 (CH), 11.22 (CH_3).

cis-1-Methyl-2-[cyclohex-3-en-1-yl]cyclopropane. ^1H NMR ($CDCl_3$) δ 5.66 (m, 2 H, C*H*=C*H*), 1.8–2.1 (m, 4 H, CH_2=CH_2), 1.2–1.6 (m, 3 H, overlapping multiplets of $CHCH_2CH_2$), 1.05 (d, *J* 5.2 Hz, 3 H, $CHCH_3$), 0.4–0.7 (m, 3 H, cyclopropyl protons *trans* to alkyl groups), −0.2 (m, 1 H, cyclopropyl proton *cis* to alkyl group).

From 6-bromo-1-hexene

cis-Isomer. ^1H NMR ($CDCl_3$) δ 3.42 (t, *J* 6.6 Hz, 2 H, CH_2Br), 1.2–2.0 (m, 6 H, CH_2's), 1.0 (d, *J* 4.6 Hz, 3 H, $CHCH_3$), 0.5–0.9 (m, 3 H, cyclopropyl protons *trans* to alkyl groups), *cis*-cyclopropyl proton off scale; *m/e* calcd. for $C_8H_{15}Br$ 190.0357, obsd. 190.0390.

trans-Isomer. ^{1}H NMR ($CDCl_3$) δ 3.40 (t, J 6.7 Hz, 2 H, CH_2Br), 1.2–2.1 (m, 6 H, CH_2's), 1.0 (d, J 5.4 Hz, 3 H, $CHCH_3$), 0.1–0.6 (m, 4 H, CH); m/e calcd. for $C_8H_{15}Br$ 190.0357, obsd. 190.0356.

From safrole

cis-Isomer. ^{1}H NMR ($CDCl_3$) δ 6.6–6.9 (m, 3 H, ArH), 5.91 (s, 2 H, OCH_2O), 2.55 (d, J 6.4, 2 H, $ArCH_2$), 1.08 (d, J 2.6 Hz, 3 H, $CHCH_3$), 0.7–0.95 (m, 3 H, cyclopropyl protons *trans* to alkyl groups), −0.2–0.0 (m, 1 H, cyclopropyl proton *cis* to alkyl groups); ^{13}C NMR ($CDCl_3$, APT) δ 147.67, 145.65, 136.72, 120.91, 108.85, 108.08 (Aromatic C), 100.68 (OCH_2O), 34.14 ($ArCH_2$), 16.89 (CH), 13.43 (CH), 12.44 ($CHCH_2$), 9.94 (CH_3); Anal. Found: C, 76.01; H, 7.65%. $C_{12}H_{14}O_2$ calcd.: C, 75.76; H, 7.42.

trans-Isomer. ^{1}H NMR ($CDCl_3$) δ 6.6–6.9 (m, 3 H, ArH), 5.91 (s, 2 H, OCH_2O), 2.46 (d, J 6.2 Hz, 2 H, $ArCH_2$), 1.04 (d, J 5 Hz, 3 H, $CHCH_3$), 0.2–0.9 (m, 4 H, CH); ^{13}C NMR ($CDCl_3$, APT) δ 147.52, 145.59, 136.24, (Aromatic C) 120.86, 108.78, 108.01 (Aromatic CH), 100.67 (OCH_2O), 39.68 ($ArCH_2$), 20.79 ($CHCH_2$), 18.82 (CH), 13.05 (CH), 13.00 (CH_3); Anal. Found: C, 75.95; H, 7.33. $C_{12}H_{14}O_2$ caldc.: C, 75.76; H, 7.42%.

From 5-hexen-2-one

cis-Isomer. ^{1}H NMR ($CDCl_3$) δ 2.53 (t, J 7.0 Hz, 2 H, $C(O)CH_2$), 2.15 (s, 3 H, CH_3CO), 1.4–1.9 (m, 2 H, $C(O)CH_2CH_2$), 1.01 (d, J 4.1 Hz, 3 H, $CHCH_3$), 0.6–0.9 (m, 3 H, cyclopropyl protons *trans* to alkyl groups), −0.35 to −0.25 (m, 1 H, cyclopropyl proton *cis* to alkyl groups); m/e calcd. for $C_8H_{14}O$ 126.1044, obsd. 126.1071.

trans-Isomer. ^{1}H NMR ($CDCl_3$) δ 2.50 (t, J 7.1 Hz), 2 H, $C(O)CH_2$), 2.14 (s, 3 H, CH_3CO), 1.3–1.8 (m, 2 H, $C(O)CH_2CH_2$), 0.99 (d, J 4.1 Hz, 3 H, $CHCH_3$), 0.1–0.6 (m, 4 H, CH); m/e calcd. for $C_8H_{14}O$ 126.1044, obsd. 126.1079.

2-(4-Cyclohexenyl)ethanol. According to Brown [30], a three-necked 250-ml flask equipped with a three-way stopcock, a reflux condenser connected to a nitrogen source and mercury bubbler, and a stopper was flushed with nitrogen and charged with 4-vinylcyclohexene (2.0 g, 18.4 mmol). The flask was vented to the mercury bubbler, and a solution of 9-BBN in tetrahydrofuran (18.4 mmol, $M = 0.38$, 49 ml) was added dropwise over 10 min. After stirring for 2 h the reaction mixture was quenched and oxidized by addition of methanol (9 ml), 1 N sodium hydroxide (6 ml) and 30% hydrogen peroxide (7.3 ml). The latter was added dropwise so that the temperature does not exceed 50°C. The mixture was allowed to cool, and then sodium chloride was added to saturate the aqueous phase. Ether was added, and the organic layer was partitioned in a separatory funnel, dried over magnesium sulfate, and concentrated in vacuo. The residue was distilled, affording 1.16 g (50%) of a clear, colorless viscous liquid: b.p. 102°C (13 torr; lit. [30] b.p. 86–87°C, 6 torr); ^{1}H NMR ($CDCl_3$) [30] δ 5.64 (m, 2 H, $CH{=}CH$), 3.70 (t, J 6.5 Hz, 2 H), 1.0–2.4 (b, 12 H).

Ethylene ketal of 5-hexene-2-one [31]. A mixture of anhydrous benzene (200 ml), ethylene glycol (130 ml) freshly distilled from sodium, and anhydrous *p*-toluenesulfonic acid (0.3 g) was placed in a 500 ml side arm flask. The flask was equipped with a Dean–Stark apparatus filled with benzene and topped by a reflux condenser attached to a drying tube, placed under nitrogen and refluxed. After 2 h, 5-hexen-2-

one (5.39 g, 60 mmol) was added via syringe. The mixture was then refluxed an additional 12 h, by which time 5 ml of water had collected, cooled, and then quenched by addition of saturated potassium carbonate (100 ml). Ether (200 ml) was added and the organic layer was extracted with water (200 ml) and saturated sodium chloride (200 ml) dried over magnesium sulfate, and concentrated in vacuo. Benzene was removed via a fractional distillation column. Distillation of the remaining yellow solution afforded 5.73 g (66.8%) of a clear, colorless liquid: b.p. 25°C (0.032 torr); ^{1}H NMR ($CDCl_3$) δ 5.5–6.0 (m, 1 H, C*H*=CH_2), 4.8–5.1 (m, 2 H, CH=CH_2), 3.92 (s, 4 H, OCH_2CH_2O), 1.6–2.3 (m, 4 H, CH_2's), 1.31 (s, 3 H, CH_3).

Methylenecycloheptane. The preparation of Oshima was followed [32]. To a 100 ml flask under nitrogen containing a suspension of zinc dust (1.77 g, 27 mmol) and methylene bromide (1.56 g, 9.0 mmol) in air-free, anhydrous tetrahydrofuran (30 ml) was added a solution of $TiCl_4$ in air-free, anhydrous methylene chloride (30 ml, 1.1 *M*, 33 mmol). An instantaneous reaction took place. The mixture turned dark green with evolution of heat. Cycloheptanone (0.67 g, 6.0 mmol) in air-free, anhydrous tetrahydrofuran (6 ml) was added dropwise after 20 min. After stirring for 21 h, the reaction was terminated by addition of water (30 ml). The organic layer was separated and washed with water (30 ml) and saturated sodium bicarbonate (30 ml), dried over magnesium sulfate and concentrated in vacuo. The residue was purified on a silica gel column and isolated by preparative GLPC: ^{1}H NMR ($CDCl_3$) [32b] δ 4.67 (t, *J* 1.0 Hz, 2 H, C=CH_2), 2.0–2.4 (b, 4 H, $(CH_2)_2$C=CH_2), 1.3–1.7 (b, 8 H, ring CH_2's).

1-Methoxy-1-cyclooctene. The preparation according to Wohl was followed [33]. A 50-ml flask was charged with cyclooctanone (3.73 g), trimethylorthoformate (1.1 equiv., 3.45 g) and *p*-toluene sulfonic acid (0.005 equiv., 0.028 g). The flask was then equipped with a reflux condenser, placed under nitrogen, and allowed to stir at 25°C. After 48 h the reaction was terminated and the condenser was replaced with a Vigreux column to distill off methanol. The Vigreux column was then replaced with a microdistillation apparatus. Distillation under reduced pressure afforded 2.88 g (70%) of a clear, colorless liquid: b.p. 71–72.5°C (14 torr, lit. [33] b.p. 70.5–71.5°C, 13 torr); ^{1}H NMR ($CDCl_3$) [33] δ 4.47 (t, *J* 8.2 Hz, 1 H, C=C*H*), 3.42 (s, 3 H, OCH_3), 1.0–2.5 (m, 12 H, CH_2's); IR 1644 (C=C).

Bicyclo[6.1.0]-9-ethyl ester. The procedure according to Akiyoshi and Matsuda [23a] was employed with the modifications of D'yakonov [23b]. A three-neck 500-ml flask was charged with cyclooctene (16.1 g) and anhydrous $CuSO_4$ (0.15 g). The flask was then equipped with a condenser, stopper, and three-way stopcock opened to a mercury bubbler, placed under nitrogen and stirred. After venting the reaction mixture through the mercury bubbler only, a solution of ethyl diazoacetate (5.7 g) in cyclooctene (4.6 g) was slowly added to the flask via automatic syringe injection and vigorous bubbling quickly ensued. The mixture turned orange-brown and after the addition was completed, the flask was heated to 135°C. The temperature was maintained through use of a thermowatch and an oil bath. After 10 h the reaction was terminated by allowing the mixture to cool to room temperature over several hours. Solid $CuSO_4$ was filtered off and washed with ether until clear. The filtrate was concentrated in vacuo yielding an orange brown solution as a mixture of ester and olefin. The methylene protons on the ethyl group appeared as a quartet at 3.8 ppm in a ^{1}H NMR spectrum of the crude ester mixture.

Bicyclo[6.1.0]-9-carboxylic acid. The crude ester mixture containing cyclooctene

was saponified by the procedure of Akiyoshi [23a]. A 500-ml flask was charged with the ester mixture, sodium hydroxide (30 g), methanol (140 ml) and water (70 ml) and then equipped with a condenser. The mixture was stirred at 70°C for 5 h and then allowed to cool to room temperature and concentrated in vacuo to remove methanol. The residue was extracted with ether to remove unreacted cyclooctene, and acidified with 10% HCl and conc. HCl until a pH of 1 was reached. Pale orange crystals slowly formed. After cooling the flask in an ice bath, the crystals were collected by filtration, washed with water and dried on a steam cone. 2.34 g of pale white, powdery crystals resulted: m.p. 110°C (lit. [23a] m.p. 113.5–114.8°C), IR 1685 (C=O), ^{1}H NMR ($CDCl_3$) δ 0.6–2.2 (15 H).

Bicyclo[6.1.0]-9-methanol. A procedure similar to those of Lane [34] and Brown [35] was followed. A 50-ml flask equipped with a reflux condenser connected to a mercury bubbler was charged with bicyclo[6.1.0]-9-carboxylic acid, (0.5 g, 2.98 mmol). The flask was then flushed with nitrogen, surrounded by a water bath, and 1.5 ml of air-free, anhydrous tetrahydrofuran was added. After the flask was vented to the mercury bubbler only, $BH_3 \cdot Me_2S$ (1.33 equiv, 10.4 *M*, 0.38 ml) was added dropwise over 5 minutes. Vigorous hydrogen gas evolution followed while the light-orange mixture was stirred at a bath temperature of approx. 23°C. The reaction was terminated after 1.5 h by the addition of 10 ml of a 1/1 water/tetrahydrofuran mixture. Vigorous hydrogen gas evolution occurred indicating destruction of excess hydride. Anhydrous potassium carbonate was added until the aqueous layer was saturated. The aqueous layer was washed with ether (3 × 10 ml). The combined organic extracts were then filtered over anhydrous magnesium sulfate and concentrated in vacuo leaving 0.34 g (74%) of a viscous, light yellow colored liquid in an isomer ratio of 2/1 *endo/exo*: ^{1}H NMR ($CDCl_3$) δ 3.71 (*exo*, d, *J* 6.3 Hz, 2 H, C*H*$_2$OH), 3.47 (*endo*, d, *J* 6.3 Hz, 2 H, C*H*$_2$OH), 0.4–0.8 (b, 3 H, C*H*), 0.8–2.4 (b, 12 H, CH_2's), (lit. NMR (CCl_4) 3.35 (*endo*, d, *J* 6 Hz), 3.56 (*exo*, d, *J* 7 Hz)) [36].

1-Phenylthio-5-hexene. A preparation similar to that for allyl phenyl sulfide was followed [37]. 6-Bromo-1-hexene (1.50 g, 9.2 mmol) was employed in place of allyl chloride. Distillation under reduced pressure resulted in 1.40 g (79.6%) of a clear, colorless liquid: b.p. 80°C (0.03 torr); ^{1}H NMR ($CDCl_3$), δ 7.0–7.5 (b, 5 H, Ar*H*), 5.5–6.0 (m, 1 H, C*H*=CH_2), 4.8–5.2 (m, 2 H, CH=C*H*$_2$), 2.91 (t, *J* 7.0 Hz, 2 H, C*H*$_2$S), 1.9–2.2 (m, 2 H, C*H*$_2$CH=CH_2), 1.4–1.9 (b, 4 H, C*H*$_2$'s). This is a previously known compound [38].

n-Propyl phenyl sulfide. The preparation for ethyl phenyl sulfide was followed. 1-Iodopropane (51.0 g, 0.30 mmol) was employed in place of ethyl iodide. Distillation under reduced pressure afforded 41.2 g (90.3%) of an opaque liquid: b.p. 68°C (0.035 torr); ^{1}H NMR ($CDCl_3$) δ 7.0–7.4 (m, 5 H, Ar*H*), 2.89 (t, *J* 7 Hz, 2 H, SC*H*$_2$), 1.61 (m, *J* 7 Hz, 2 H, C*H*$_2$CH$_3$), 1.01 (t, *J* 7 Hz, 3 H, C*H*$_3$).

α-Chloropropyl phenyl sulfide. The preparation for α-chloroethyl phenyl sulfide was followed. n-Propyl phenyl sulfide (6.0 g, 39 mmol) was employed in place of ethyl phenyl sulfide. Distillation yielded 3.9 g (53% of a clear, colorless liquid: b.p. 83°C (0.3 torr); ^{1}H NMR ($CDCl_3$) δ 7.2–7.6 (m, 5 H, Ar*H*), 5.20 (t, *J* 6.3 Hz, 1 H, SC*H*), 2.09 (q, *J* 7 Hz, 2 H, C*H*$_2$), 1.13 (t, *J* 7 Hz, 3 H, C*H*$_3$).

*η^5-Cyclopentadienylbis(carbonyl)(1-phenylthiopropyl)iron(II) (**10**).* The preparation of **8** was followed. α-Chloropropyl phenyl sulfide (5.56 g, 14.9 mmol) was employed in place of α-chloroethyl phenyl sulfide. Purification by modified [16] flash chromatography, resulted in 4.52 g (65%) of a dark brown oil. An NMR sample under

nitrogen was prepared in the normal manner: ^{1}H NMR ($CDCl_3$) δ 6.9–7.4 (m, 5 H, Ar*H*), 4.90 (2, 5 H, C_5H_5), 3.68 (dd, *J* 7.0 Hz, 1 H, FeC*H*), 1.5–2.0 (m, 2 H, CH_2), 0.95 (t, *J* 7.1 Hz, 3 H, CH_3). After recrystallizing the oil several times with air-free, anhydrous pentane, 3.4 g (48%) of yellow crystals were obtained: ^{1}H NMR ($CDCl_3$) δ 6.9–7.4 (m, 5 H, Ar*H*), 4.90 (s, 5 H, C_5H_5), 3.68 (dd, *J* 7.0 Hz, 1 H, FeC*H*), 1.5–2.0 (m, *J* 7 Hz, 2 H, CH_2), 0.95 (t, *J* 7 Hz, 3 H, CH_3).

1-Phenylthio-1-propene (11). This compound formed as a byproduct of the failed cyclopropanation reactions between **10**, magic methyl and olefins in *p*-dioxane at 60°C. Following the workup used for the ethylidene transfer reactions, **11** was isolated by preparative GLPC: ^{1}H NMR ($CDCl_3$) δ 7.0–7.4 (b, 5 H, ArH), 5.7–6.4 (m, 2 H, C*H*=C*H*), 1.8 (dd, *J* 1 Hz, 3 H, CH_3). This same compound formed upon decomposition of $PhSCHClCH_2CH_3$, and is a previously known compound [39].

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