Vinyl Grignard Reagents. Rearrangement of the Cyclopropylidenephenylmethylmagnesium Bromide

Jean-Luc Derocque* and Freyja-Beate Sundermann

Institut für Organische Chemie, Universität des Saarlandes, 66 Saarbrücken, West Germany

The reactions of cyclopropylidenephenylmethyl bromide (I-Br), 1-phenyl-2-methylpropenyl bromide (V-Br), and 2-phenylcyclobutenyl bromide (III-Br) with magnesium in diethyl ether (DEE) and tetrahydrofuran (THF), and with organotin hydrides, were investigated. The 2-phenylcyclobutenylmagnesium bromide (III-Mg) was found to be stable, while the cyclopropylidenephenylmethylmagnesium bromide (I-Mg) yielded the ring-cleavage product 4-phenylbut-3-ynylmagnesium bromide (II-Mg). A radical-like and a four-centered cyclic reaction mechanism are proposed for the ring-cleavage reaction.

Adjacent aryl groups and double bonds are able to stabilize cations, radicals, and anions by delocalization through their π-orbital(s) system. It has been extensively shown in the literature that stabilization of a cation by a cyclopropyl substituent may be greater than that by a vinyl group.[1]

The question of the influence of a cyclopropyl substituent on an adjacent anion, or a carbon–metal bond, has also been raised.[2] From the results published in the literature it can be concluded that stabilization exists and may be observed especially if additional effects, such as conjugative stabilization through phenyl ring(s)[2f,g] or nonconjugative stabilization in the α-cyclopropylvinyl Grignard reagent,[3] are also present. This ability has been attributed to the low-lying vacant MO of the cyclopropyl bond (conjugative stabilization) and to the relatively high s character of bonds from a cyclopropyl substituent, which should raise its electronegativity (nonconjugative stabilization).[2j]

Therefore it seems reasonable to us that the cyclopropylidenephenylmethyl anion (I⁻) would be a stable species, as is the case for the corresponding cation.[4] Since intramolecular additions of organometallic compounds to double and triple bonds have often been reported,[2,5] we expected that, if 4-phenylbut-3-ynylmagnesium bromide (II-Mg) would cyclize, the cyclopropylidenephenylmethyl Grignard reagent (I-Mg) would be preferable to the 2-phenylcyclobutenyl Grignard reagent (III-Mg). Although the ring strain for the formation of I-Mg would greatly increase the energy of the transition state, our suggestion was reinforced by the fact that cyclopropylphenylcarbinyl metal species are true intermediates in the rearrangement of homoallyllic Grignard reagents.[2f,g] Moreover, in addition to the stabilization of the carbon–metal bond in I-Mg by the phenyl and the cyclopropyl ring, cyclization of II-Mg to the vinylic Grignard reagent I-Mg might be favored to the extent that the energy of the transition state could reflect the greater stability of the sp² compared to the sp³ carbon–metal bond in II-Mg.

However, we observed[6] that 4-phenylbut-3-ynylmagnesium bromide (II-Mg) did not rearrange to any of the cyclic products I-Mg or III-Mg by refluxing in THF.

We aim to discuss here the comparative stability of the vinylic Grignard reagents I-Mg and III-Mg (Scheme I).

Results and Discussion

Cyclopropylidenephenylmethylmagnesium Bromide and Radical. Cyclopropylidenephenylmethyl bromide (I-Br) was added with a standard (xylene mixture) to a suspension of magnesium (5% excess) preheated at the desired temperature in the solvent (THF or DEE) in a nitrogen atmosphere. After the reaction had started, samples were pipetted out at time intervals and quenched with D₂O. Glc and glc–mass spectral analysis led to the fol-

Scheme I[a]
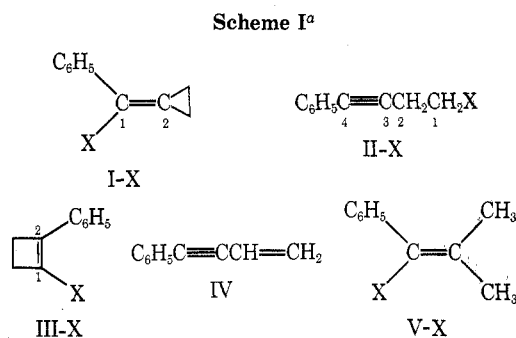
[a] In the text the reference number of a compound followed by symbols (Mg for –MgBr, –Br, –H, –D, etc.) or by the radical or the anion signs describes that compound with the corresponding substituent instead of X.

lowing observations (see Tables I and II and Scheme II). During the formation of the Grignard reagent I-Mg, four other products are formed along with I-Mg: cyclopropylidenephenylmethane (I-H), 4-phenylbut-3-ynylmagnesium bromide (II-Mg), 1-phenylbutyne (II-H), and 1-phenylbut-3-enyne (IV).

After it has been generated in the medium, the concentration of I-Mg decreases while the concentrations of 4-phenylbut-3-ynylmagnesium bromide (II-Mg) and cyclopropylidenephenylmethane increase, showing that I-Mg undergoes two competitive reactions: a ring cleavage rearrangement to form II-Mg and a hydrogen–metal exchange reaction with the solvent or other species present in the medium, yielding the hydrocarbon I-H. A further slow decrease of the deuterium incorporation in the II-H–II-D mixture shows that 4-phenylbut-3-ynylmagnesium bromide (II-Mg) abstracts hydrogen to give the corresponding
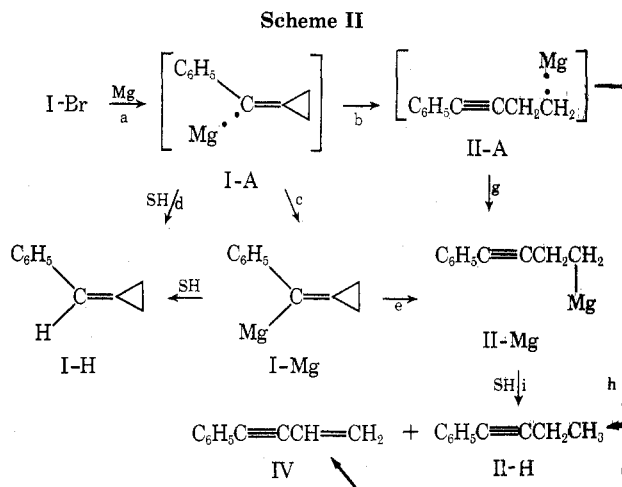
Scheme II

Table I
Distribution[a] of the Products Formed during the Generation of the Grignard Reagent I-Mg and after 20–25-hr Reaction Time

Run	Solvent	Temp, °C	Time	% I-Mg	% I-H	% II-Mg	% II-Hg	% IV	% of the ring cleavage
1	THF	66	c	34	25	30	4	7	41
			b	0	25	12	60	3	75
2	THF	37	c	56	19	12	3	10	25
			b	0	42	1	48	9	58
3	DEE	37	c	19	24	31	20	6	57
			b	0	37	1	58	4	63

[a] In percentages measured from the gas chromatogram of the mixtures. Standard deviation: ±5% of the given value. [b] After 20–25-hr reaction time. [c] About 10–15 min after the addition of the bromide, when most of the magnesium had disappeared.

Table II
Rates[a] of Ring-Cleavage Reaction and Hydrogen–Metal Exchange of I-Mg and II-Mg after They Have Been Generated in the Medium

Run	Solvent	Temp, °C	k_e for I-Mg $\longrightarrow$ II-Mg	k_f for I-Mg $\longrightarrow$ I-H	k_i for II-Mg $\longrightarrow$ II-H
1	THF	66	1.7×10^{-4}	b	1.7×10^{-5}
2	THF	37	3.6×10^{-5}	1.2×10^{-5}	
3	DEE	37	4.1×10^{-5}	4.1×10^{-5}	6.4×10^{-5}

[a] Standard deviation: ±15% of the given value, k in reciprocal seconds. [b] The hydrogen–metal exchange of I-Mg is much slower than the ring-cleavage reaction (k_c) and the concentration of I-H remains constant (see Table I).

hydrocarbon (II-H). As for the 1-phenylbut-3-enyne (IV) formed during the reaction of cyclopropylidenephenyl-methyl bromide (I-Br) with magnesium, its concentration remains constant at the beginning and then decreases slowly, probably because of further polymerization under the conditions of the reaction. Remarkable is the relatively high rate of formation of the hydrocarbons I-H and II-H at the beginning of the reaction, while the rates of hydrogen abstraction from the solvent by I-Mg and II-Mg decrease considerably after they have been generated in the medium (see Tables I and II).[7] Measurement and calculation of the rate constants for these different processes (see Table II) indicates that the rate of rearrangement of the cyclopropylidenephenylmethylmagnesium bromide (I-Mg) to the open-chain Grignard reagent II-Mg is little influenced by changing from THF to DEE (see runs 2 and 3, Table II). In refluxing THF (run 1) the ring cleavage (k_e) is much faster than the abstraction of hydrogen from the solvent (k_f), and the concentration of cyclopropylidene-phenylmethane (I-H), which has been formed during the generation of the Grignard reagent I-Mg, remains constant.[8] Thus in boiling THF the only reaction of I-Mg to take place is the ring-cleavage reaction.

From our results it appears, therefore, that two different processes account for the rearrangement of the forming and the already formed Grignard reagent I-Mg.

Since evidence is accumulating that radicals are true intermediates in the formation and further reaction of Grignard compounds,[9] radical-induced reactions (and rearrangement when possible) are expected to occur, at least partially, during the formation of Grignard reagents. This is compatible with the same order of intramolecular cyclization ability which has been found during the formation of unsaturated Grignard reagents and when the corresponding radicals were generated from the halides with tin hydrides.[10] It was therefore of interest to study the behavior of both cyclopropylidenephenylmethyl radical (I°) and 4-phenyl-3-ynyl radical (II°). Crandall and Keyton[11] observed no intramolecular cyclization of the homopropargyl radical generated from 4-phenylbut-3-ynyl bromide (II-Br) with tributyltin hydride. We have reinvestigated their experiment and our results confirm their observation. Cyclopropylidenephenylmethyl radicals (I°)

were generated from I-Br and tributyltin hydride in DEE at room temperature. After 15 min, glc analysis of the ethereal solution showed the presence of 1-phenylbutyne (II-H) and cyclopropylidenephenylmethane (I-H) in the ratio of 9:1, and a small amount (1–2%) of 1-phenylbut-3-enyne (IV). The high percentage of 1-phenylbutyne (II-H) is not surprising on account of the known instability of cyclopropylcarbinyl radicals[12] and the higher stability of alkyl radicals compared to that of the vinyl radicals[13] under the conditions of the reaction. The presence of cyclopropylidenephenylmethane (I-H, 9%) might be due to some stabilization of the radical I° by the adjacent phenyl group which enhances its lifetime and permits its reaction with a hydrogen radical before rearranging to the 4-phenylbut-3-ynyl-radical (II°). This was supported by increasing the hydrogen radical concentration in the reaction mixture through addition of thiophenol or by carrying out the reaction in neat tributyltin hydride. The corresponding II-H/I-H ratios were 4:1 for these two reactions (see Experimental Section, Table III). In all these experiments no 1-phenylcyclobutene (III-H) could be detected in the gas chromatograms of the reaction mixtures.

In another run, tributyltin deuteride was added dropwise to a solution of I-Br in refluxing THF. Glc–mass spectral analysis of the solution showed that no hydrogen incorporation in the 4-deuterio-1-phenylbutyne (II-D) was detectable under the conditions of measurement but that the cyclopropylidenedeuteriophenylmethane (I-D) contained 7–10% of the undeuterated hydrocarbon (I-H). Thus abstraction of hydrogen from the solvent (THF) by the cyclopropylidenephenylmethyl radicals probably does occur, at least partially. Small quantities of deuterated cyclopropylphenylmethane and deuterated 1-phenylbut-1-ene could be detected in the reaction mixture.[14]

The extensive ring cleavage to form the 4-phenylbut-3-ynylmagnesium bromide (II-Mg) and the simultaneous formation of the disproportionation product 1-phenylbut-3-enyne (IV) along with 1-phenylbutyne (II-H) found during the generation of cyclopropylidenephenylmethylmagnesium bromide (I-Mg) are comparable with the products obtained in the radical-induced reaction of cyclopropylidenephenylmethyl bromide (I-Br) with tributyltin hydride.

Three distinctly different types of mechanism may be reasonably conceived for the intramolecular cyclization and the related ring-cleavage reaction of organometallic compounds:[15] (a) the polarized covalent carbon–metal bond may ionize to a carbanion, which then rearranges; (b) the carbon–metal bond may dissociate to an univalent metal species and a free radical which undergoes rearrangement before recombination; (c) a concerted cyclic process may occur, induced by the formation of a metal π complex in which changes in carbon–carbon bonding occur simultaneously with transfer of the metal from one carbon to another.

According to our results (Scheme II) it seems reasonable to discuss the process of ring cleavage that we observed *during the formation of the Grignard I-Mg* in terms of a radical-induced mechanism. The occurrence or non-occurrence of a radical-induced ring-closure reaction is one based on orbital overlap consideration. For ring closure to be favorable, the p orbital containing the odd electron and the orbital of the multiple bond must be close enough together and of proper orientation for good overlap to take place. For ring cleavage, a similar orbital overlap requirement is also necessary between the orbitals of the radical and the breaking carbon–carbon bond. This has been emphasized by the results of Friedrich and Holmstead[16] on the direction of ring opening in the benzobicyclo[4.1.0]hepten-2-yl radical. It is evident that this orbital overlap is maximal for ring opening in the cyclopropylidenephenylmethyl radical (I°). The ring-cleavage reaction must also be energetically favored owing to ring-strain release in the transition state and the greater stability of primary radicals compared to vinyl radicals.[13]

To explain our results we have envisaged the pathways shown in Scheme II, which are based on the mechanism proposed by Walborsky and Young.[17]

During the one-electron transfer from magnesium to halogen a reactive radical pair I-A is formed, which may react further according to three distinct pathways: (a) it can collapse to the more stable Grignard reagent I-Mg where the bonding electrons have reorganized themselves to form a carbon–metal bond; (b) it can undergo a ring-cleavage reaction to form the open-chain radical pair II-A [the latter can either disproportionate to form 1-phenylbut-3-enyne (IV) and 1-phenylbutyne (II-H), collapse to the Grignard reagent II-Mg, or abstract hydrogen to form II-H]; (c) I-A can also abstract a hydrogen radical to form I-H.

The Grignard reagent I-Mg *when formed* undergoes further ring cleavage to the more stable primary Grignard reagent II-Mg, but with a rate constant smaller than that observed for the similar rearrangement from the reactive species I-A. I-Mg can also abstract hydrogen from the solvent to yield I-H and it *is the relative rates of these two competitive reactions which determine the I-H:II-H ratio at the end of the reaction, i.e.,* when no more cyclopropylidenephenylmethylmagnesium bromide (I-Mg) is present in the mixture (see Table I, footnote b). At the end, 4-phenylbut-3-ynylmagnesium bromide (II-Mg) abstracts hydrogen to form II-H.

The formation of 4-phenylbut-3-ynylmagnesium bromide from cyclopropylidenephenylmethylmagnesium bromide could also be explained through an equilibrium between I-A and I-Mg. However, this would have increased simultaneously the concentration of I-H, II-H, and IV in the same proportion as that observed during the formation of the Grignard reagent I-Mg. We found that this was not the case and that the concentration of 1-phenylbut-3-enyne (IV) remained unchanged. Moreover, the rate of disappearance of cyclopropylidenephenylmethylmagnesium bromide (I-Mg) in refluxing THF equals that of

appearance of 4-phenylbut-3-ynylmagnesium bromide (II-Mg).

Since an equilibrium between the species I-A and I-Mg must be excluded, another process must account for the further rearrangement of I-Mg to II-Mg. The small rate difference observed for the ring-cleavage reaction by replacing DEE with a solvent of higher dielectric constant, such as THF (see Table II, runs 2 and 3), is not compatible with an ionic mechanism in which a large variation in charge separation takes place when going from the ground state to the transition state. A concerted four membered ring process similar to the one proposed by Hill and Davidson[15] seems to be much more consistent with our results. In this process the energies which are necessary to form the common activated complex from the open-chain and cyclic products depend, among other factors, on the distance between the four interacting atoms. Measurements on Dreiding models of the average distances between these atoms in the homoallyl–cyclopropylcarbinyl and homopropargyl–cyclopropylidene systems gave the following results [Scheme III, L (average) = $(a + b + c + d)/4$].

Scheme III
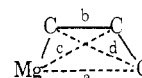
	L		L	ΔL
Homoallyl	2.90 Å	Cyclopropylcarbinyl	2.82 Å	0.08
Homopropargyl	3.02 Å	Cyclopropylidene	2.50 Å	0.52

In the homoallyl–cyclopropylcarbinyl rearrangement the change in average distances is small relative to that in the homopropargyl–cyclopropylidene system (about six times greater for the latter). The geometry change between ground state and transition state must thus be much more important for the latter compared to the former and cyclization must require more drastic conditions. Moreover, in the cyclopropylidenemethyl Grignard reagent I-Mg the four centers are even closer together (2.5 Å) than in the cyclopropylcarbinyl system (2.82 Å) and the interaction between the orbitals, and thus the change in bondings, must be favored to form the open-chain product II-Mg.

The total rearrangement of cyclopropylidenephenylmethylmagnesium bromide (I-Mg) to the open-chain compound II-Mg and the irreversibility of this process does, however, not necessarily reflect the absence of stabilization of the adjacent vinyl carbon–metal bond by the cyclopropylidene substituent in I-Mg. For this a comparison with the properties of the homologous 1-phenyl-2-methylpropenylmagnesium bromide (V-Mg) should be worthwhile.

We may indeed assume that the more stable a Grignard reagent, the faster the radical pair (for instance I-A, Scheme II) will collapse to the Grignard (I-Mg), and consequently the concentration of the corresponding hydrocarbon (I-H) formed during that process (pathways c and d, Scheme II) will be smaller. In other words, the more stable the Grignard reagent, the smaller the ratio for the rate constants k_d/k_c. By deuterolysis of the Grignard mixtures from the cyclopropylidenephenylmethyl bromide (I-Br) and from the 1-phenyl-2-methylpropenyl bromide (V-Br) in refluxing THF just after most of the magnesium had disappeared in the solution, the ratios I-H:I-Mg and V-H:V-Mg were 0.74 and 0.18, respectively. This shows that the collapse reaction of the radical pairs I-A and V-A to the Grignards I-Mg and V-Mg is four times faster for compound V than for I. It could be objected that this difference reflects only the greater ability of the radicals I° to

abstract protons compared to that of radicals V°. However, in the hydrogen-abstraction reactions of cyclopropylidenephenylmethyl bromide (I-Br) and 1-phenyl-2-methylpropenyl bromide (V-Br) with tributyltin deuteride in refluxing THF, the ratios I-H:I-D and V-H:V-D were found to be 0.1–0.08 and 0.08–0.06, respectively, indicating that, at the worst, I° abstracts hydrogen 1.6–1.7 times faster than V°. By taking this into consideration, it still gives a rate constant 2.5 times larger for the collapse reaction of the radical pair V-A to the Grignard reagent V-Mg, compared to that of radical pair I-A to the Grignard I-Mg. This result would mean that, of the two Grignards I-Mg and V-Mg, the latter is more stable, and therefore that there is no stabilizing effect of the cyclopropylidene substituent on the adjacent carbon–metal bond in cyclopropylidenephenylmethylmagnesium bromide (I-Mg).

This surprisingly contradicts the weak stabilization observed elsewhere on metal–carbon bonds by conjugative interaction with a cyclopropane ring.[2,3] According to recent INDO calculations, Danen[18] concluded that, in general, C–C hyperconjugation is more favorable than C–H hyperconjugation in cationic and radical species, while the reverse is true for carbanions. If some correlations may exist in the causes of stabilization of metal–carbon bond and anionic charge, the irreversible isomerization of homoallenyl Grignard reagents to α-cyclopropyl vinyl Grignard reagents[3] might therefore be due to the partial stabilization of the metal–carbon bond through C–H rather than C–C hyperconjugation. Such an influence is indeed excluded in the cyclopropylidene system I.

It is a well-known fact that vinyl anions and carbon atoms in vinyl organometallic compounds are sp^2 hybridized and that vinyl metal compounds are geometrically stable.[19] Consequently, in the Grignard compound I-Mg the orbital of the carbon–magnesium bond interacts only with one of the two carbon–carbon bond orbitals of the adjacent cyclopropane ring. This must induce an *unsymmetrical* delocalization of the charges in the ring, which favors its opening, and this is in contrast with the symmetrical delocalization of the charges in the cyclopropylidene cation.

For the nonconjugative stabilization of the cyclopropyl ring on adjacent anion and carbon–metal bonds, it has been proposed that the relatively high s character of the bonds from a cyclopropyl substituent should raise its electronegativity.[2j] If this is true for the C_1–C_2 bond in I-X, which may have a hybridization between sp^2 and sp, there is no apparent reason for the hybridization of the carbon–metal bonding to have a higher s character. On the contrary, higher s character of the C_1–C_2 bonding should raise the p character in the C_1–metal orbital and therefore decrease its electronegativity and thus the stabilization of a negative charge (or negative polarization) on that carbon atom.[20]

2-Phenylcyclobutenylmagnesium Bromide, Radical, and Anion. Only 1-phenylcyclobutene (III-H) is formed by hydrolysis of the reaction mixture from 2-phenylcyclobutenyl bromide (III-Br) and magnesium in boiling THF or DEE. Deuterolysis of the Grignard solution in refluxing THF after most of the metal had disappeared yielded the corresponding hydrocarbon with 80–85% deuterium incorporation (III-D). By refluxing further in the same solvent we observed a slow decrease of the III-D:III-H ratio ($k = 5.8 \times 10^{-5} \pm 0.5$),[7] showing that 2-phenylcyclobutenylmagnesium bromide (III-Mg) had exchanged its metal for hydrogen.

III-Br does not react at room temperature with either tributyltin or triphenyltin hydride in DEE or undiluted. Without solvent, a slow reaction takes place at higher temperature (80–100°) and yields 1-phenylcyclobutene

(III-H) as the main product along with some phenylcyclobutane (5–10%).[14] No trace of isomeric compounds (such as I-H and/or II-H) was detectable in the gas chromatograms of the reaction mixtures. The slow reactions observed with tin hydride suggest a relatively high energy of activation in the transition state for the formation of the 2-phenylcyclobutenyl radical (III°) and are comparable with the small rate constants that we have reported for the solvolysis reaction of III-Br.[4]

Treatment of 2-phenylcyclobutenylmagnesium bromide (III-Mg) in THF with mercury(II) bromide gave the 2-phenylcyclobutenylmercuric bromide (III-HgBr), which has been isolated and characterized. III-HgBr was treated at 0° with a suspension of K/Na alloy[2g] in THF. Only 1-phenylcyclobutene (III-H, 80–90%) and phenylcyclobutane (20–10%) were formed by hydrolysis after 15 min.[21] The concentration of both compounds was decreased by stirring further the reaction mixture at 0°. Only polymeric materials were formed and at no time could we detect any other isomeric species which could have been derived from rearrangement of the 2-phenylcyclobutenyl anion (III^-).

From the preceding results it appears that 2-phenylcyclobutenyl Grignard reagent (III-Mg), anion (III^-), and radical (III°) are stable under the conditions of their generation or at least do not rearrange to other isomeric species. In those systems the substituents are not in an appropriate position for stabilization, nor are orbitals with high energy (such as the carbon–carbon bond orbitals of the four-membered ring) in a geometrically favorable position for good overlap which could initiate the rearrangement of the products.

Also the geometry required by the four-membered ring increases the s character of the orbital corresponding to the C–X bond in III-X. This must favor the stabilization (nonconjugative) of the negative charge in III^- and of the negative polarization in the corresponding metal compound III-Mg. It explains also the high activation energy for the formation of the 2-phenylcyclobutenyl radical (III°), the odd electron of which must be in a high energy level owing to the large s character of that orbital.

Conclusions

Of the two cyclic metal species (I-Mg and III-Mg) which could have reasonably resulted from the intramolecular rearrangement of the homopropargyl Grignard reagent II-Mg, 2-phenylcyclobutenylmagnesium bromide (III-Mg) was found to be the more stable. It was, however, found elsewhere[6] that II-Mg does not rearrange to III-Mg, probably because the linear geometry requirement of the triple bond in II-Mg prevents "effective" interaction between orbitals at the C_1 and C_4 atoms. It appears thus that in the intramolecular addition process of organometallic compounds to triple bonds a chain length of at least three atoms[10] is necessary between the unsaturated center and the metal–carbon bond.

Attempts to observe cyclization of the homopropargyl anion II^- generated from the 4-phenylbut-3-ynylmercuric bromide (II-HgBr) and K/Na alloy[2g] have been unsuccessful owing to the occurrence of competitive reactions.[22,23]

Experimental Section

Table III

Compd	% in DEE	% in DEE in presence of thiophenol	% in pure *n*-Bu$_3$SnH
I-H	9	19	20
II-H	90	76	80
IV	1	5	

Analytical Methods. Glc–mass spectral analyses were performed with a Mat-311 Varian mass spectrometer combined with a gas chromatograph, using a 10 ft × 0.125 in. 10% Carbowax 20M column. Deuterium incorporation in hydrocarbons was evaluated from the mass spectra of the compounds by repeated cyclic scans between m/e 100 and 140. Calculations were performed on average values obtained for the peak intensities in the region of the molecular peaks and in the region corresponding to the fragmentation of the methyl and/or CH$_2$D group. Pure undeuterated compounds were obtained as described before[4] and pure deuterated substances were synthesized from the bromides and organotin deuteride (see below). Mass spectral analysis by the decelerating voltage method showed that the deuterium incorporation was equal to or higher than 99.5%. In two cases the hydrocarbons formed after deuterolysis of the Grignard mixtures were separated by preparative gas chromatography. Measurement and calculation of the deuterium incorporation in these hydrocarbons either by glc or direct injection through the inlet system of the mass spectrometer gave identical results, showing that there is sensibly no separation of deuterated and undeuterated species under the gas chromatographic conditions employed.

Reaction with Magnesium Metal. The reaction vessel, containing 10% excess of magnesium, was flame dried in a nitrogen stream. The solvent was added and the mixture was preheated at the desired temperature under a nitrogen atmosphere. A solution of the bromide in the corresponding solvent was added dropwise with a standard (xylene mixture) to the stirred magnesium suspension. Aliquots were pipetted out at time intervals, quenched with D$_2$O (99.9%), and analyzed by glc and glc–mass spectral methods as described above.

Reaction with Organotin Hydride (and Deuteride). In a general procedure a solution of the bromide was added dropwise to an equimolecular solution of the organotin compound in the same solvent (THF or DEE). The mixture was stirred at room temperature until no more starting material was present (about 15–30 min for I-Br and V-Br) and the mixture was analyzed by glc (10 ft × 0.125 in. 10% Carbowax column). The solvent and product(s) were distilled under vacuum and purified further by preparative glc when necessary. Whenever the reactions were carried out in neat materials a 20% excess of organotin material was used. This method was employed for the preparation of the deuterated hydrocarbons from the bromides I-Br, II-Br, and V-Br with tributyltin deuteride.

Cyclopropylidenephenylmethyl Bromide (I-Br). Glc analysis of the reaction mixture of I-Br with tributyltin hydride gave the following results (Table III).

In another run a solution of tributyltin deuteride was added dropwise to a solution of I-Br in refluxing THF. Glc–mass spectral analysis gave the following hydrogen ratios for the undeuterated and deuterated hydrocarbons formed during the reaction: I-H:I-D = 0.08–0.1; II-H:II-D = 0 (no hydrogen was detectable under the condition of the analysis).

1-Phenyl-2-methylpropenyl Bromide (V-Br). In an identical run with the one described above in refluxing THF but with V-Br as starting material the ratio V-H:V-D was found to be 0.06–0.08.

2-Phenylcyclobutenyl Bromide (III-Br). III-Br does not react at room temperature with tributyltin hydride and it takes about 20 hr for the reaction to be completed in *neat* materials at 80°. The 1-deuterio-2-phenylcyclobutene (III-D) was prepared from bromide III-Br and triphenyltin deuteride as follows. A 210-mg (1 mmol) portion of III-Br and 700 mg of triphenyltin deuteride were mixed in a distillation apparatus and heated at 100° under vacuum (3–4 Torr), the receiving flask being cooled at 0°. The reaction was stopped when no more substance distilled (about 15–20 hr). Analysis of the distillate showed that it corresponded to a mixture of deuterated cyclobutane (5–10%)[14] and 1-deuterio-2-phenylcyclobutene (III-D, 90%). III-D was purified by preparative gas chromatography and was found to contain more than 99.6% of deuterium.

2-Phenylcyclobutenylmercuric Bromide (III-HgBr). A mixture of 4 g of 2-phenylcyclobutenyl bromide (III-Br) and 0.5 g of magnesium in 40 ml of absolute THF was refluxed in a nitrogen

atmosphere until no more starting material was present (glc, 6 ft × 0.125 in. 10% Silicone column). The solution was cooled to room temperature, decanted from the excess of magnesium, and added dropwise at room temperature under nitrogen to a stirred suspension of 7.5 g of HgBr$_2$ in absolute THF (15 ml). The mixture was then refluxed for 2 hr, stirred for 24 hr at room temperature, and treated with 5% aqueous acetic acid. After addition of ether the organic layer was decanted, washed with water, and dried over sodium sulfate. Solvents were distilled off under vacuum and the residue was purified by crystallization in petroleum ether (bp 30–60°)-ether mixture or ethanol (white cristals, mp 114–116°): nmr (CDCl$_3$) δ 2.62 (m, 2 H), 3.17 (m, 2 H) (these two multiplets are symmetrical), 7.42 (m, 5 H); mass spectrum m/e 410–412 (molecular peak), 129 (100% peak).

Reaction of 2-Phenylcyclobutenylmercuric Bromide with K/Na Alloy.[2g] A solution of 100 mg of 2-phenylcyclobutenylmercuric bromide in 15 ml of absolute THF was added at 0° in a nitrogen atmosphere to a stirred suspension of K/Na alloy (40 mg K/8 mg Na) in 15 ml of absolute THF containing a standard (diisoamyl ether). Samples were pipetted out at intervals and carefully quenched in a nitrogen atmosphere with an ethanol–water mixture. Glc analysis showed the presence only of phenylcyclobutene (III-H, 95%) and phenylcyclobutane (5%), but the concentrations of both compounds decreased with time to about one-third of the initial concentration after 3 hr. No traces of isomeric species (such as I-H or II-H) were detectable in the gas chromatogram of the reaction mixture at any time. A polymeric residue was obtained by working up the reaction mixture after 10–15 hr.

References and Notes

(1) (a) B. A. Howell and J. G. Jewett, *J. Amer. Chem. Soc.*, **93**, 798 (1971); (b) M. Hanack, *Accounts Chem. Res.*, **3**, 209 (1970); (c) M. Hanack and H.-J. Schneider, *Angew. Chem., Int. Ed. Engl.*, **6**, 666 (1967); (d) T. Bässler and M. Hanack, *Tetrahedron Lett.*, 2171 (1971); (e) W. E. Heyd and M. Hanack, *Angew. Chem.*, **85**, 318 (1973).

(2) (a) S. Silver, P. R. Schafer, J. E. Nordlander, and J. D. Roberts, *J. Amer. Chem. Soc.*, **82**, 2646 (1960); (b) P. T. Lansbury, V. A. Pattison, W. A. Clement, and J. D. Silver, *ibid.*, **86**, 2247 (1964); (c) D. J. Patel, C. L. Hamilton, and J. D. Roberts, *ibid.*, **87**, 5144 (1965); (d) D. J. Cram, "Fundamentals in Carbenion Chemistry," Academic Press, New York, N. Y., 1965, Chapter 6, pp 211–222; (e) E. L. McCaffery and S. W. Shalaby, *J. Organometal. Chem.*, **3**, 101 (1965); (f) M. E. H. Houden, A. Maercker, and J. D. Roberts, *J. Amer. Chem. Soc.*, **88**, 1732 (1966); (g) A. Maercker and J. D. Roberts, *ibid.*, **88**, 1742 (1966); (h) E. L. McCaffery and S. W. Shalaby, *J. Organometal. Chem.*, **8**, 17 (1967); (i) J. A. Landgrebe and J. D. Shoemaker, *J. Amer. Chem. Soc.*, **89**, 4465 (1967); (j) M. J. Perkins and P. Ward, *Chem. Commun.*, 1134 (1971).

(3) (a) H. G. Richey and W. C. Kossa, *Tetrahedron Lett.*, 2313 (1969); (b) M. Santelli and M. Bertrand, *C. R. Acad. Sci., Ser. C* **271**, 757 (1970).

(4) J.-L. Derocque, F.-B. Sundermann, N. Youssif, and M. Hanack, *Justus Liebigs Ann. Chem.*, 419 (1973).

(5) (a) E. A. Hill, H. G. Richey, Jr., and T. C. Rees, *J. Org. Chem.*, **28**, 2161 (1963); (b) S. A. Kandill and R. D. Dessy, *J. Amer. Chem. Soc.*, **88**, 3027 (1966); (c) H. G. Richey and T. C. Rees, *Tetrahedron Lett.*, 4297 (1966); (d) H. R. Ward, *J. Amer. Chem. Soc.*, **89**, 5517 (1967); (e) H. G. Richey and A. M. Rothman, *Tetrahedron Lett.*, 1457 (1968); (f) E. A. Hill, R. J. Theissen, A. Doughty, and R. Miller, *J. Org. Chem.*, **34**, 3681 (1969); (g) E. A. Hill and H. R. Ni, *ibid.*, **36**, 4133 (1971).

(6) J.-L. Derocque, U. Beisswenger, and M. Hanack, *Tetrahedron Lett.*, 2149 (1969).

(7) One of the referees has pointed out that inadvertently introduced moisture was very probably responsible for the high rates found for the reactions of Grignard reagents with solvents. We have been also surprised by the magnitude of these values, but the quite good reproducibility of our results and also the same order of rates found for the reactions of III-Mg and V-Mg with solvents let us suppose that the introduction of moisture was constant and therefore our results were still valuable for a comparative study. In all our experiments the same batch of magnesium metal and the same source of nitrogen were used.

(8) We found that the hydrogen–metal exchange reaction of I-Mg and II-Mg were faster in DEE than in THF (see Table II). Similar results have been reported in the literature: A. Maercker and N. Theyson, *Justus Liebigs Ann. Chem.*, **759**, 132 (1972); H. M. Walborsky and M. S. Aronoff, *J. Organometal. Chem.*, **51**, 31 (1973).

(9) (a) H. R. Ward, R. G. Lawber, and T. A. Marzilli, *Tetrahedron Lett.*, 521 (1970); (b) H. W. H. J. Bodewitz, C. Blomberg, and F. Bickelhaupt, *ibid.*, 281 (1972).

(10) W. J. Michaely, Ph.D. Thesis, Indiana University, Bloomington, Ind. We would like to thank Professor J. K. Crandall for communication of his results prior to publication.

(11) J. K. Crandall and D. J. Keyton, *Tetrahedron Lett.*, 1653 (1969).

(12) (a) C. Walling and P. S. Fredricks, *J. Amer. Chem. Soc.*, 84, 3326 (1962); (b) J. K. Kochi, P. J. Krusic, and D. R. Eaton, *ibid.*, 91, 1877, 1879 (1969); (c) R. A. Sheldon and J. K. Kochi, *ibid.*, 92, 4395 (1970).

(13) J. E. Bennet, B. Mile, A. Thomas, and B. Ward, *Advan. Phys. Org. Chem.*, 8, 1 (1970).

(14) The formation of saturated hydrocarbons has been reported in the reaction of olefinic compounds with tin hydrides: (a) M. Pereyre and J. Valack, *Tetrahedron Lett.*, 489 (1969); (b) F. G. A. Stone and R. West, *Advan. Organometal. Chem.*, 1, 47 (1964); (c) E. C. Friedrich and R. L. Holmstead, *J. Org. Chem.*, 37, 2546 (1972).

(15) E. A. Hill and J. A. Davidson, *J. Amer. Chem. Soc.*, 86, 4663 (1964).

(16) E. C. Friedrich and R. L. Holmstead, *J. Org. Chem.*, 37, 2540 (1972); see also ref 14c.

(17) H. M. Walborsky and A. E. Young, *J. Amer. Chem. Soc.*, 86, 3288 (1964).

(18) W. C. Danen, *J. Amer. Chem. Soc.*, 94, 4835 (1972).

(19) (a) A. S. Drieding and R. J. Pratt, *ibid.*, 76, 1902 (1954); (b) H. Normant and P. Maitte, *Bull. Soc. Chim. Fr.*, 1439 (1956); (c) D. Seyferth and L. G. Vaughan, *J. Amer. Chem. Soc.*, 86, 883 (1964); (d) M. Tamura and J. Kochi, *Int. J. Methods Syn. Org. Chem.*, 303 (1971).

(20) (a) D. E. Applequist and D. F. O'Brien, *J. Amer. Chem. Soc.*, 85, 743 (1963); (b) R. M. Salinger and R. E. Dessy, *Tetrahedron Lett.*, 729 (1963).

(21) The reductive addition of alkali metals to the activated double bond of the phenylcyclobutenyl system (III-X) must be responsible for the formation of phenylcyclobutane.

(22) J.-L. Derocque and F.-B. Sundermann, accepted for publication in *J. Org. Chem.*

(23) Z. Csuros, P. Caluwe, and M. Szwarc, *J. Amer. Chem. Soc.*, 95, 6171 (1973).

(24) G. J. M. Van Der Kerk, J. G. Noltes, and J. G. H. Suijten, *J. Appl. Chem.*, 7, 366 (1957).

(25) H. G. Kuivila and D. F. Beumel, *J. Amer. Chem. Soc.*, 83, 1246 (1961).

Effects of Alkyl Substituents in the Chromic Acid Oxidation of Tetralins

John W. Burnham,[1a] William P. Duncan,[1b] and E. J. Eisenbraun*

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74074

Gary W. Keen and Mynard C. Hamming

Research and Development Department, Continental Oil Company, Ponca City, Oklahoma 74601

The chromic acid oxidation of a series of mono- and polyalkyl-1,2,3,4-tetrahydronaphthalenes was investigated. Preferential oxidation occurs at the benzylic methylene position para to an alkyl substituent in the aromatic ring. An alkyl group ortho to a benzylic methylene position may enhance or retard oxidation at that position, depending upon the degree of steric crowding by the alkyl group. 2-Alkyltetralins also undergo preferential oxidation in that 3-alkyl-1-tetralones predominate in the product mixture.

Chromic acid oxidation of hydrocarbons has been intensively studied. In general, for aliphatic hydrocarbons, the relative rates of oxidation in primary, secondary, and tertiary CH positions are 1:110:7000.[2] Although considerable data exist concerning the oxidation of aromatic–aliphatic systems,[3] very little information is available on oxidation of hydrocarbons containing nonequivalent benzylic positions capable of competing for the oxidizing agent. Linstead[4a] and Ghosal[4b] showed that a pronounced electronic effect is operative in the oxidation of 6-methoxytetralin to 6-methoxy-1-tetralone.

The mechanism of chromic acid oxidation of hydrocarbons has been extensively investigated.[2,3,4b,4c] A current rationalization utilizes an initial hydrogen abstraction to give a resonance hybrid of (a) an alkyl radical–Cr(V) complex and (b) a carbonium ion–Cr(IV) complex.[5,6] Since the rates of oxidation of hydrocarbons have been shown to parallel those for solvolysis of the corresponding tosylates, a carbonium ion intermediate is further implicated.[7a] It has been concluded that steric hindrance is not important in chromic acid oxidation of alkylcyclohexanes.[7b]

This study of the chromic acid oxidation of tetralins was prompted by an earlier observation that some alkyltetralins may be converted to 1-tetralones in high yield with considerable selectivity and thereby provide otherwise less accessible ketones.[8a] We previously utilized chromic acid in the conversion of indans to indanones in high yields.[8b]

The data presented in Table I provide ample evidence that an electronic effect is operative in the oxidation of tetralins substituted with alkyl groups in the aromatic ring. This is apparent from the ratio of product tetralones 3b:3c (1.0:1.3) and 4b:4c (2.7:1.0). Comparison of the lat-

ter ratio to those of 7b:7c (2.9:1.0) and 10b:10c (2.4:1.0) shows that the methyl, ethyl, and *tert*-butyl group have about the same electronic effect. The electronic effect responsible for the ratio of products obtained from 3a and 4a is manifest throughout the series in Table I. Steric effects result from alkyl groups at the peri position of the aromatic ring or from an alkyl group adjacent to a potential carbonyl site (C-2) in the saturated ring. The latter effect is illustrated by the products from 2a, 5a, and 8a (methyl, ethyl, *tert*-butyl). The most obvious effect, steric and electronic, is shown by the products obtained in the oxidation of 6a and 9a compared to the products from 3a (effects of peri alkyl groups) as well as by a comparison of the oxidation of 12a and 13a *vs.* 14a and 15a (methyl *vs.* *tert*-butyl groups). The ratio of products 16b:16c (1.0:24) from 16a suggests that the effects of 2-alkyl and peri alkyl groups are synergistic.

A diminution, owing to steric influence of methyl at C-2, appears in the ratio of products obtained from oxidation of 4a and 12a, the ratio decreasing from 2.7:1.0 to 2.0:1.0. Comparison of the ratios of 1-tetralones obtained from 10a, 14a, and 15a indicate a very pronounced alkyl (*tert*-butyl) steric effect at the C-2 position. As expected, this effect decreases in changing from *tert*-butyl to methyl for 4a, 12a, and 13a.

The alkyl groups in the aromatic ring may have a pronounced electronic influence on the ratio of 1-tetralones, as evidenced by comparison of the products from 3a, 11a, and 17a, in which 3c, 11c, and 17c predominate over 3b, 11b, and 17b despite possible steric interference of the methyl group at the peri position. However, this effect is reversed for 6a and 9a (as expected) owing to the increased bulk of the ethyl and the *tert*-butyl group, and