On the Mechanism of 1-Phenylcyclobutene Formation in the Reaction of 1-Chloro-4-bromo-1-phenyl-1-butene with Magnesium[1]

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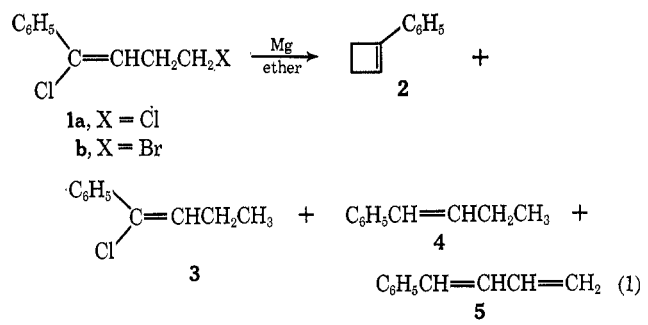
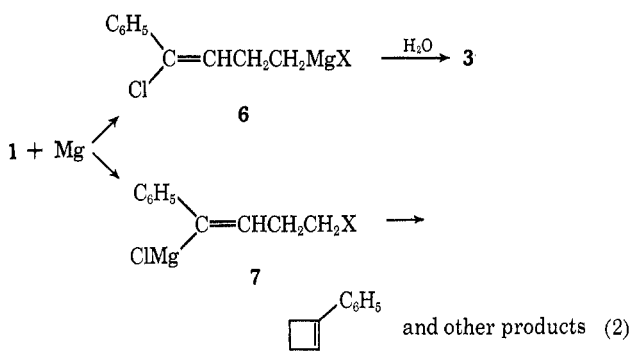
A mechanism previously proposed for formation of 1-phenylcyclobutene from the reaction of 1,4-dihalo-1-phenyl-1-butene is shown to be unacceptable, since a proposed intermediate Grignard reagent (**6**) is stable under the reaction conditions. Among several possibilities considered, a radical cyclization mechanism appears to be the most likely.

In 1965, Newman and Kaugars[2] reported that 1,4-dichloro-1-phenyl-1-butene (**1a**) reacts with magnesium in ether to produce a product mixture including 1-phenylcyclobutene (**2**), *trans*-1-chloro-1-phenyl-1-butene (**3**), *cis*- and *trans*-1-phenyl-1-butene (**4**), and 1-phenyl-1,3-butadiene (**5**) (eq 1). They proposed the

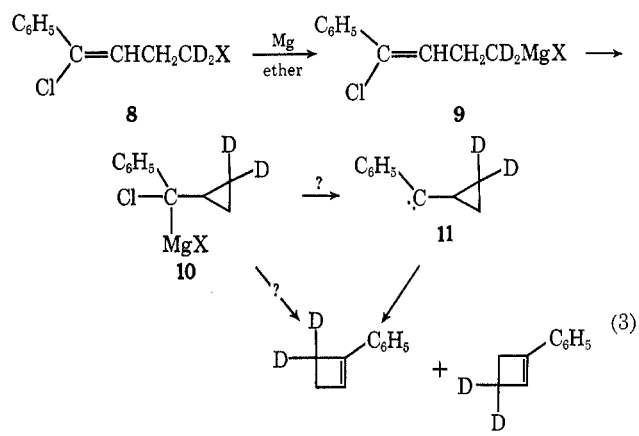


mechanism shown in eq 2. Largely because **2** did not



increase at the expense of **3** with longer reaction times, they concluded that, once formed, primary Grignard reagent **6** does not undergo any further reaction until hydrolysis. Then, other products were thought to be formed from a vinylic Grignard reagent **7**. The phenylcyclobutene may be explained by an internal nucleophilic displacement in **7**. From yields of products, the rather surprising conclusion was reached that the vinylic Grignard reagent **7** is formed more rapidly than primary Grignard **6**.

More recently, Fry and Moore[3] reinvestigated this reaction. They found by a deuterium labeling experiment that the phenylcyclobutene is formed by a pathway that results in scrambling of carbon atoms 3 and 4. A pathway including intermediate carbenoid **10** or carbene **11** was proposed (eq 3). Experiments in our



laboratories, to be published shortly, suggest a similar mechanism for cyclobutene formation from 1-chloro-4-bromo-1-butene. However, this mechanism again raises the question as to why the yield of **3** remains constant. Fry and Moore were forced to conclude that a portion of the primary Grignard reagent **6** must abstract a proton from some other species present in the reaction mixture, in competition with its cyclizing rearrangement.

Results and Discussion

At the time that the report of Fry and Moore was published, we were also engaged in a reinvestigation of the Newman and Kaugars reaction. Since alkyl bromides form Grignard reagents more readily than alkyl chlorides, the use of **1b** should almost exclusively produce primary Grignard reagent **6**. Hence, by the Newman–Kaugars mechanism, little or no phenylcyclobutene should have formed. However, it remained a major product of the reaction. A deuterium labeling experiment with **1b** had also led to results similar to those of Fry and Moore, again requiring a product-determining precursor for **2** with essential equivalence of carbon atoms 3 and 4.

However, additional results also exclude the mechanism of Fry and Moore. Specifically, primary Grignard reagent **6**, *once formed*, does not rearrange readily to phenylcyclobutene (**2**), and most of the 1-chloro-1-phenyl-1-butene (**3**) is formed only upon final hydrolysis of the reaction solution. Hence, **6** cannot be an intermediate in the formation of **2**. This crucial point is demonstrated by the following experiments, which are reported in detail in the Experimental Section.

A solution prepared from **1b** and magnesium in ether was found by examination of the nmr spectrum to con-

(1) We gratefully acknowledge support of the research by the Petroleum Research Fund, administered by the American Chemical Society.

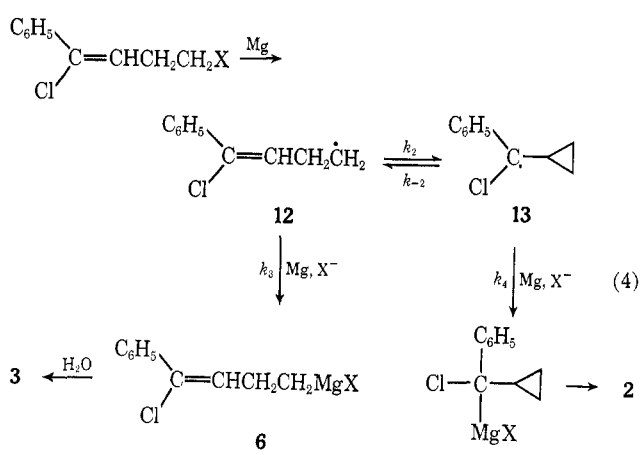
(2) M. S. Newman and G. Kaugars, *J. Org. Chem.*, **30**, 3295 (1965).

(3) A. J. Fry and R. H. Moore, *ibid.*, **33**, 425 (1968).

tain both phenylcyclobutene and a primary Grignard reagent. Extraction of the mixture with pentane removed the former but left the latter. Additional heating of the residual Grignard in ether solution produced more phenylcyclobutene, but only slowly at 115°. This is far too slow to account for its presence as a major product after only a few minutes' reflux in ether or tetrahydrofuran during preparation of the reagent. A portion of Grignard solution was hydrolyzed with deuterium oxide. The spectrum of 1-chloro-1-phenyl-1-butene isolated showed at least 75% (and probably nearly 95%) of one deuterium in the methyl group (smaller amounts of 1-phenyl-1-butene isolated from the same reaction were also largely monodeuterated in *both* 1 and 4 positions). Therefore, it may be safely concluded that the major Grignard reagent present was indeed **6**.

The present results, then, appear to exclude both the mechanisms of Newman and Kaugars[2] and of Fry and Moore.[3] Several previously unconsidered possibilities exist. First of all, it is possible that the mechanism is indeed a Grignard cyclization, as proposed by Fry and Moore, but that the cyclization involves an initially formed active Grignard reagent species, which is in part deactivated to ordinary Grignard. Bryce-Smith[4] notes that alkylation of aromatic rings by an initially formed, possibly unsolvated and monomeric, Grignard reagent occurs much more readily than with a pre-formed reagent in hydrocarbon solution. A similar species might be involved in the present instance. A related possibility is that a free carbanion, which might be an intermediate in Grignard formation, is the unstable, rearranging intermediate.

A second possibility is shown in eq 4. A free radical, likely an intermediate in the formation of Grignard reagent, may cyclize and subsequently be reduced by



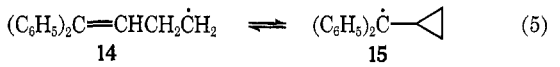
(4)

the magnesium. Similar mechanisms have been proposed for cyclizations from acetylenic halides upon reaction with magnesium[5] or alkyllithium[5,6] reagents. Reasonable routes to the other products reported by Newman and Kaugars, 1-phenyl-1-butene (**4**) and 1-phenyl-1,3-butadiene (**5**), might be hydrolysis of the di-Grignard from the dihalide and a dehydrohalogenation, respectively. The latter product was not identified in the present study.

(4) D. Bryce-Smith and B. J. Wakefield, *Tetrahedron Lett.*, 3295 (1964).
(5) J. L. Deroegue, U. Beisswenger, and M. Hanack, *ibid.*, 2149 (1969).
(6) H. R. Ward, *J. Amer. Chem. Soc.*, **89**, 5517 (1967).

In this mechanism, partition between the two pathways may occur at either of two stages. First, if equilibrium between radicals **12** and **13** is attained, then the relative yields of products by the two pathways will depend upon the equilibrium constant for their interconversion and the relative rates of further reduction of the two radicals (k_3 and k_4). On the other hand, if $k_4 \gg k_{-2}$, k_2 is effectively irreversible. Then the product-determining partition is between k_2 and k_3.

There is substantial precedent for rapid equilibrium cyclization of 3-buten-1-yl radicals. Roberts and coworkers have found that the rearrangement shown in eq 5 is extremely rapid.[7] The relative yields of the hydrogen-abstraction products of the two radicals at 125° are independent of the concentration of the very effective hydrogen atom donor, triethyltin hydride. Equilibration of the methylene groups of **14** also was complete. With triethyltin hydride at 125°, the ratio of products derived from **14** and **15** was about 14:1.



(5)

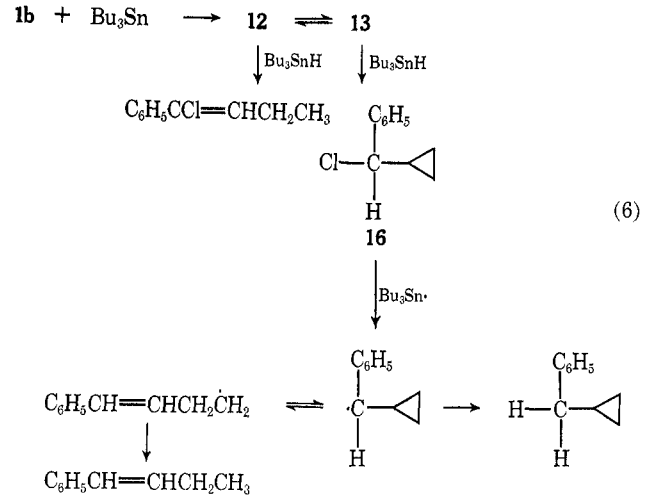
The Grignard reagent corresponding to **14** reacts with oxygen or cobaltous chloride, by mechanisms believed to involve free radicals, to yield 66 and 12% of cyclized products, respectively.[8] Since the new bond formed by **14** should be stronger than the one formed by **15**, it is probable that **14** reacts more rapidly than **15**. Therefore, though there is no quantitative basis for an estimate of the equilibrium constant, **15** is surely an important, if not the major, constituent. While the chlorine atom in radical **13** should not stabilize the radical as effectively as the second phenyl in **15**, it is still reasonable that substantial amounts of **13** may be present at equilibrium. It is also possible that electron transfer to **13** may be particularly enhanced by the conjugated π-orbital system. In other related studies, smaller amounts of cyclized products appear to be formed from substituted cyclopropylmethyl radicals lacking resonance stabilization.[9]

A consequence of rapid equilibration of radicals **12** and **13** is that the methylene groups in the labeled halide **8** should become scrambled in Grignard reagent **6**. The nmr spectrum of the solution formed from **8** with magnesium has a broadened singlet resonance at the position expected for the CH_2Mg group, but it only accounts for 20% of two hydrogens. Therefore, we must conclude that radicals **12** and **13** do not attain equilibrium. Reduction of cyclized radical **13** occurs more rapidly than its ring opening, so that radical lifetimes during the Grignard formation stage must be quite short.

In order to learn more of the behavior of radical **12**, we have briefly studied the reaction of **1b** with tri-*n*-butyltin hydride. Cyclization of the radical before hydrogen abstraction from the hydride would lead to phenylcyclopropylmethyl chloride (**16**). This might

(7) T. A. Halgren, M. E. H. Howden, M. E. Medof, and J. D. Roberts, *ibid.*, **89**, 3051 (1967).
(8) M. E. Howden, A. Maercher, J. Burdon, and J. D. Roberts, *ibid.*, **88**, 1732 (1966).
(9) L. K. Montgomery and J. W. Matt, *ibid.*, **89**, 934 (1967).

be expected to undergo further reduction itself at a rate competitive with that of **1b** (eq 6). Evidence was

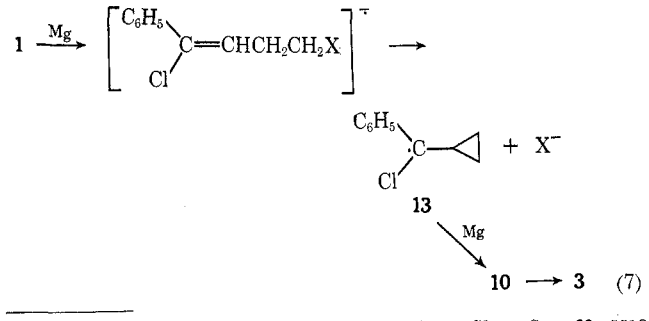


(6)

not found in the nmr spectrum for any cyclopropane products. However, 1-phenyl-1-butene was identified in quantities about 10–20% as much as the 1-chloro-1-phenyl-1-butene in a run with 1 *M* tri-*n*-butyltin hydride. Abstraction of a vinylic chlorine would not be expected to compete effectively with that of the primary bromine of **1b**; so we conclude that any 1-phenyl-1-butene present must have been formed by the route shown in eq 6. In control experiments, 1-phenyl-1-butene did not react at all under the conditions used, and 1-chloro-1-phenyl-1-butene appeared to produce some *n*-butylbenzene, by a route not presently understood, with very little 1-phenyl-1-butene.

Another reaction in which radical intermediates appear to be generated from alkyl halides is in the reaction with alkyllithium compounds.[10] When **1b** reacts with excess methyllithium in tetrahydrofuran, a vigorous reaction ensues, and 1-phenylcyclobutene is the only identified product. The same reaction with deuterated bromide produced 1-phenylcyclobutene with C_3 and C_4 scrambled. A mechanism may be proposed similar to that of eq 4, but with methyllithium rather than magnesium acting as the electron source. In a reaction between **1b** and butyllithium in hexane–ether, carried out in the probe of a T-60 nmr spectrometer, the CIDNP spectrum of 1-butene[10a] was detected. No enhanced absorption or emission attributable to phenylcyclobutene was observed, but the complexity of the product and the relatively small amount of phenylcyclobutene might be responsible for the lack of observation.

An alternative mechanism for formation of 1-phenylcyclobutene is shown in eq 7. In this instance, the



(7)

three-membered ring is generated in an irreversible step, an internal nucleophilic displacement of halide by the styrene-type radical anion. The entry to the possible equilibrium **12** ⇄ **13** now occurs through **13**. If ring opening of **13** is slow relative to its further reduction ($k_4 > k_{-2}$), then a competing normal Grignard formation would explain the observed result of limited scrambling of carbons in primary Grignard **6**. A similar mechanism could explain phenylcyclobutene formation in the methyllithium reaction. An argument against this mechanism is that both the internal displacement and Grignard formation should be affected by the change from bromine to chlorine in **1a**. It would be surprising that approximately the same balance of reaction paths should be found from both compounds.

Newman and Kaugars also found that 1,4-dichloro-1,2-diphenyl-1-butene yielded 90% of 1,2-diphenylcyclobutene on reaction with magnesium in ether. It is reasonable to presume that reaction follows a mechanism similar to the 1-phenylcyclobutene formation in the present study.

Experimental Section

Nmr and ir spectra were run on a Varian Associates HA-100 spectrometer and a Beckman IR-8 spectrometer, respectively. Gas chromatography was carried out on an Aerograph A-90-P chromatograph, with columns of Dow Hi-vac silicone grease and QF-1 on Chromosorb P.

1-Chloro-4-bromo-1-phenyl-1-butene.—Aluminum chloride (40.7 g, 0.31 mol) was added in portions to 4-bromobutanoyl chloride (52.2 g, 0.30 mol) in 200 ml of benzene. The mixture was refluxed for 15 min more and poured over ice, and the organic product was worked up by distillation: bp 113–117° (0.4 mm); nmr (CCl_4) δ 2.20 (quintet, 2, J = 6.5 Hz), 3.06 (t, 2, J = 6.5 Hz), 3.45 (t, 2, J = 6.5 Hz), 7.2 (m, 3), and 7.85 ppm (m, 2). The product (25 g, 0.11 mol) was allowed to react with phosphorus pentachloride (31.4 g, 0.15 mol) in 80 ml of carbon tetrachloride. The reaction mixture was poured over ice, and the product was taken up in benzene and distilled. After a forerun consisting largely of phosphorus oxychloride, a major product fraction, bp 105–110° (0.4 mm), was collected. Redistillation yielded a center cut: bp 111–112° (0.85 mm); nmr (CCl_4) δ 2.88 (q, 2, $J \sim 6.9$ Hz), 3.37 (t, 2, J = 6.9 Hz, CH_2Br), 6.10 (t, 1, J = 6.9 Hz, =CH), 7.15 (m, 3, aromatic), and 7.5 ppm (m, 2, aromatic). Chemical shifts were concentration dependent. A weak triplet at δ 5.9 may perhaps be attributed to a few per cent of the cis isomer.

Anal. Calcd for $C_{10}H_{10}ClBr$: C, 48.91; H, 4.11. Found: C, 49.17; H, 4.17.

1-Chloro-4-bromo-1-phenyl-1-butene-*4,4-d*$_2$.—4-Chloro-4-phenyl-3-buten-1-ol-*1,1-d*$_2$ was prepared in a manner similar to that described by Fry and Moore.[3] To the alcohol (3.2 g) and pyridine (0.6 g), phosphorus tribromide (1.4 g) was added dropwise with cooling on an ice bath. The mixture was heated 2 hr at 100°, hydrolized with water, extracted with ether, dried, and distilled. The nmr spectrum of the product was similar to that of the undeuterated compound, but the absorption at δ 2.9 was a broadened doublet ($J \cong 7$ Hz) and the absorption at δ 3.37 was completely absent (<2%). Triplets in the olefinic region at δ 6.12 and 5.92 ppm and an extra methylene absorption at δ 2.58 ppm indicated a mixture of isomers in a ratio of about 6:1. Undeuterated chloro bromide was prepared in this fashion with similar results.

1-Phenyl-1-butene was prepared as described by Newman and Kaugars. Cis and trans isomers were separated by gas chromatography, with the cis isomer eluted first: nmr (CCl_4) (cis) δ 1.09 (t, 3, J = 7.5 Hz, CH_3), 2.33 (quintet, 2, $J \sim 7.5$ Hz, CH_2), 5.6 (triplet of doublets, 1, J = 7.2 11.5 Hz, olefinic), 6.34 (d, 1, J = 11.7 Hz, olefinic), and 7.19 ppm (s, 5, aromatic); (trans) δ 1.10 (t, 3, J = 7.5 Hz, CH_3), 2.21 (m, 2, J = 7.5, 5 Hz, CH_2), 6.2 (m, 2, olefinic), and 7.2 ppm (m, 5, aromatic).

1-Chloro-1-phenyl-1-butene was prepared as described by Newman and Kaugars. Cis and trans isomers were separated

(10) (a) H. R. Ward and R. G. Lawler, *J. Amer. Chem. Soc.*, **89**, 5518 (1967); (b) D. Bryce-Smith, *J. Chem. Soc.*, 1603 (1956).

by gas chromatography, with the cis isomer eluted first: nmr (CCl_4) (cis) δ 1.04 (t, 3, J = 7.3 Hz, CH_3), 2.14 (quintet, 2, $J \sim 7.3$ Hz, CH_2), 5.88 (t, 1, J = 7.5 Hz, olefinic), and 7.29 ppm (m, 5, aromatic); (trans) δ 1.12 (t, 3, J = 7.5 Hz, CH_3), 2.40 (quintet, 2, $J \sim 7.2$ Hz, CH_2), 6.04 (t, 1, J = 6.9 Hz, olefinic), and 7.2 and 7.5 ppm (m, 3 and 2, aromatic).

1-Phenylcyclobutene.—We are grateful for a sample received as a gift from Dr. M. McKinney of Marquette University: nmr (CCl_4) δ 2.47 (m, 2, CH_2), 2.73 (m, 2, CH_2), 6.17 (t, 1, olefinic, J = 1.2 Hz), and 7.0–7.5 ppm (m, 5, aromatic). It was found that samples appeared to polymerize on standing for several days, and, on some occasions, isomerization or polymerization appeared to occur during gas chromatography. Since well-defined peaks were obtained, it appears that reaction may have occurred in the detector.

Reaction of 1-Chloro-4-bromo-1-phenyl-1-butene with Magnesium.—A Grignard reagent was prepared from 1.32 g (5.4 mmol) of the chloro bromide and 0.214 g (8.9 mg-atoms) of magnesium in 4 ml of ether. The magnesium was a sublimed grade obtained from the Dow Metal Products Co., and the ether was freshly distilled from lithium aluminum hydride under a flow of nitrogen. The nmr spectrum of this solution showed a somewhat broadened triplet at δ −0.37 ppm (J = 8.5 Hz) attributable to the CH_2Mg protons, and a triplet at δ 6.33 ppm (J = 7 Hz), attributable to the olefinic hydrogens of the primary Grignard reagent **6**. A tight olefinic triplet at δ 6.17 ppm (J = 1.2 Hz) and allylic methylene absorption at δ 2.47 and 2.76 ppm correspond to the spectrum of 1-phenylcyclobutene. Additional, poorly defined, olefinic absorption was present from δ 5.8 to 6.2 ppm. The spectrum remained unchanged on heating for up to 4 hr at 60°. Hydrolysis produced a mixture of products identified by gc retention times and nmr spectra as follows (relative yields in parentheses): *cis*-1-phenyl-1-butene (0.03), *trans*-1-phenyl-1-butene (0.10), 1-phenylcyclobutene (0.53), *cis*-1-chloro-1-phenyl-1-butene (0.11), and *trans*-1-chloro-1-phenyl-1-butene (1.00). Yields varied in different preparations. This was in part a consequence of a tendency of the 1-phenylcyclobutene to polymerize on standing. 1-Phenyl-1,3-butadiene[2] was not identified, though some minor fractions of short retention time were not investigated.

Solvent was distilled from the Grignard reagent under high vacuum, the semisolid residue was stirred with 3 ml of pentane, and the pentane was removed by syringe. After four such extractions, residual pentane was pumped off and replaced by fresh diethyl ether. The spectrum ascribed to phenylcyclobutene was no longer visible, while the absorptions at δ 6.33 and −0.37 ppm remined, as did some poorly defined olefinic resonances. The solution was heated for periods up to 4 hr at 115° in a sealed nmr tube. At the end of this time, the δ 6.33 and −0.37 ppm absorptions were decreased by about 50%, and the olefinic triplet of 1-phenylcyclobutene was the most prominent peak in the rather cluttered olefinic region. The nmr spectrum of the pentane extract clearly showed the presence of 1-phenylcyclobutene; additional absorption could be attributed to *trans*-1-chloro-1-phenyl-1-butene, and gas chromatography showed that the two components were present in a mole ratio of about 4:1. It is likely that much of the latter results from hydrolysis of some Grignard reagent entrained in the pentane extract, since the extract became cloudy on standing in air or addition of water. Hydrolysis of the remaining Grignard solution (not heated) gave mainly 1-chloro-1-phenyl-1-butene, along with smaller amounts of 1-phenyl-1-butene (1:0.2) and a trace of phenylcyclobutene.

A sample of Grignard solution was hydrolyzed with deuterium oxide, and the products were isolated by gas chromatography. The *trans*-1-chloro-1-phenyl-1-butene had aromatic and olefinic resonances similar to those of undeuterated material. The methyl absorption consisted of a 1:2:1 triplet of 1:1:1 triplets, corresponding to a vicinal J_{H-H} = 7.7 Hz and a geminal J_{H-D} = 1.9 Hz, respectively. The low-field component of each of the H–D triplets was slightly enhanced, and the splitting slightly reduced, suggesting the triplet corresponding to undeuterated material, and an up-field shift of about 0.017 ppm produced by geminal isotopic substitution. The methylene resonance was a broadened quartet. The ir spectrum showed C–D absorption at 2180 cm^{-1}. From nmr integrals and comparison of intensities within the methyl multiplet, it was concluded that the sample was 80–95% monodeuterated. The spectrum of the cis isomer was generally similar in appearance, but there was an insufficient amount for a quantitative analysis. The spectrum of the *trans*-1-phenyl-1-butene was similar in appearance in the methyl region but with probably 20% of undeuterated material. Integration of the olefinic and aromatic regions indicated 70–80% of one vinyl deuterium.

A sample of a reaction solution was stirred for 5 days under nitrogen, in the presence of excess magnesium, and hydrolyzed with deuterium oxide. None of the products were substantially deuterated, suggesting that little Grignard reagent remained. The product was significantly enhanced in 1-phenylcyclobutene. It is not certain whether this is a consequence of conversion of other products to phenylcyclobutene under the influence of magnesium or simply to destruction of the Grignard reagents present in a manner not leading to simple hydrolysis (as by reaction with oxygen).

In a reaction with undeuterated halide in tetrahydrofuran, the nmr of the reaction solution showed CH_2Mg proton resonance at δ −0.42 ppm, somewhat weaker and less well resolved than in diethyl ether. There was a very broad absorption at δ 0.4 ppm, and the olefinic triplet of the primary Grignard reagent **6** was weak or absent. The presence of phenylcyclobutene was clear. The mixture was extracted with pentane as before. The extract contained phenylcyclobutene as the major identifiable product (from nmr), but there was a substantial amount of unidentified material, largely lacking in olefinic absorption and probably polymeric. The remaining Grignard reagent was hydrolyzed with deuterium oxide. The nmr spectrum of the product mixture indicated a CH_2CH_2D group and an olefinic triplet, along with much other ill-defined absorption. Gas chromatography showed more 1-phenyl-1-butene than in the ether reaction. It is likely, judging from the spectra, that the Grignard solution contained largely the di-Grignard reagent.

Reaction of 1-Chloro-4-bromo-1-phenyl-1-butene-*4,4-d*$_2$ with Magnesium.—The reaction of 1 g of the halide with 0.16 g of magnesium in 4 ml of ether was carried out as with the undeuterated halide. The nmr spectrum of the original reaction solution was similar to that obtained previously with two exceptions: the methylene resonances of 1-phenylcyclobutene were collapsed into a pair of broadened singlets, and the $-CH_2Mg$ resonance was weak (about 20% of two protons, based on olefinic resonance) and was a broadened singlet. The mixture was extracted with pentane as before. The extract had broadened singlets at δ 2.47 and 2.73 ppm; the lack of splitting is consistent with assignment to the methylene resonances of 1-phenylcyclobutene-4,4-d_2 and -3,3-d_2, respectively. Since the higher field resonance was wider, it was assigned to the 4,4-d_2 isomer; the three-bond vinyl–allylic coupling of cyclobutene is known to be greater than the four-bond coupling.[11] The olefinic resonance appeared to be a superposition of the triplet (J = 1.3 Hz) for the 4,4-d_2 isomer and a singlet, shifted δ 0.010 ppm to higher field, for the 3,3-d_2 isomer. The two isomers were present in nearly equal amounts (±10%). The residual Grignard solution had an olefinic triplet, most probably attributable to the primary Grignard reagent **6**-d_2, and a variety of weaker, ill-defined bands in the olefinic region.

Reaction of 1-Chloro-4-bromo-1-phenyl-1-butene with Alkyllithium Reagents.—To 1 g of the chloro bromide in 10 ml of tetrahydrofuran was added 12 ml of a 1.8 M solution of methyllithium in ether. The reaction refluxed spontaneously. Toward the end of the addition, a long-lasting blue color was generated in the solution. The mixture was hydrolyzed with water and gas chromatographed. The major component was identified as 1-phenylcyclobutene. Similar reactions occurred with butyllithium.

The experiment was repeated with the deuterated chloro bromide. The crude product was distilled to a cold finger under aspirator vacuum. Its nmr spectrum was similar to that of the deuterated phenylcyclobutene isolated from the magnesium reaction, indicating a mixture of 3,3-d_2 and 4,4-d_2 isomers.

The reaction of **1b** with butyllithium was carried out in an nmr tube in an attempt to observe chemically induced dynamic nuclear polarization (CIDNP). In an nmr tube were placed 40 μl of chloro bromide **1b**, 0.25 ml of 1.6 M butyllithium in hexane, and 0.035 g of diphenylacetylene. The nmr spectrum was scanned on a T-60 spectrometer and 100 μl of ether was added. Rapid scanning of the spectrum showed the appearance of positive and negative peaks similar to those observed in the analogous reaction with 1-bromobutane.[10a] These signals decayed and within about 4 min the spectrum remained constant. It appeared to have signals corresponding to olefinic protons of 1-butene and 1-

(11) E. A. Hill and J. D. Roberts, *J. Amer. Chem. Soc.*, **89**, 2047 (1967).

phenylcyclobutene, along with other olefinic resonances. No transient abnormalities were apparent in the position of the 1-phenylcyclobutene absorption.

Reactions with Tri-*n*-butyltin Hydride.—In an nmr tube, there were placed 0.55 ml of a 1.2 *M* stock solution of tri-*n*-butyltin hydride in benzene, 0.144 g (0.59 mmol) of 1-chloro-4-bromo-1-phenyl-1-butene, 0.0016 g of azobisisobutyronitrile, and 0.020 ml of tetrahydrofuran (as an internal reference). The sample was heated at 85° until the nmr spectrum showed complete disappearance of the Sn–H band (δ 2.24 ppm upfield from benzene). The nmr spectrum showed partial disappearance of the chlorobromide olefinic triplet δ 1.32 ppm upfield from benzene, and replacement by a new triplet at δ 1.28 ppm. By gas chromatography, components of the mixture were separated and identified as *cis*-1-phenyl-1-butene (by retention time), *trans*-1-phenyl-1-butene (by nmr), *cis*-1-chloro-1-phenyl-1-butene (by nmr), *trans*-1-phenyl-1-chloro-1-butene (by nmr), and cis and *trans* isomers of the starting halide (by retention time). The ratio of *trans*-1-phenyl-1-butene to *trans*-1-chloro-1-phenyl-1-butene was about 0.1. Reactions at lower concentrations gave less complete reduction and apparent side reactions.

A similar attempt at reduction of 1-phenyl-1-butene led to no disappearance of either hydride or alkene, based on nmr observation. With 1-chloro-1-phenyl-1-butene, disappearance of the hydride occurred, and a product was formed which was identified by nnr and by its retention time as *n*-butylbenzene. 1-Phenyl-1-butene was formed in less than 10% of the amount of *n*-butylbenzene.

A competitive reaction was carried out with 1-bromobutane and 1-phenyl-1-chloro-1-butene. No 1-phenyl-1-butene was found by gas chromatography.

Registry No.—**1b**, 28273-63-4; 4,4-dideuterio-**1b**, 28273-64-5; **2**, 3365-26-2; *cis*-**3**, 28273-67-8; *trans*-**3**, 3365-30-8; *cis*-**4**, 1560-0-94; *trans*-**4**, 1005-64-7.

Conformational Analysis. LXXII. Solvolysis Studies with the 5-Phenylcyclooctanol System[1-3]

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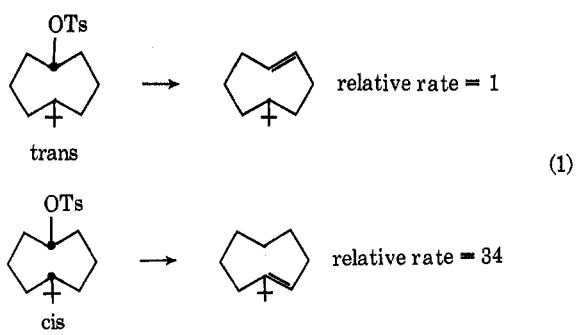
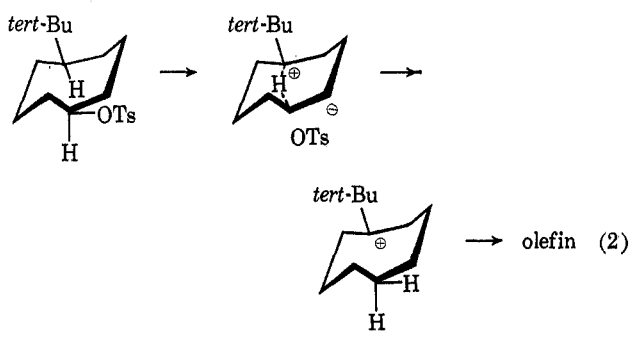
A rate and product study has been carried out on the solvolysis in aqueous ethanol of *cis*- and *trans*-5-phenylcyclooctanol tosylate and the corresponding *p*-anisyl derivatives. The results indicate that in these compounds, and by inference other cyclooctyl derivatives, neighboring group participation is not of importance in determining solvolysis rates. The rather fast rates observed, and rate differences between isomers, are attributed to steric effects.

Transannular hydride shifts across medium rings have been known for almost 20 years.[5] In an effort to understand the stereochemical features of these shifts, the solvolyses of a number of different stereoisomers of three- and five-substituted cyclooctane compounds were studied.[6-10] It was found that *cis*-5-*tert*-butylcyclooctyl tosylate solvolyzed much more rapidly than did the trans isomer, and the product obtained from the cis isomer was mostly rearranged olefin, while that from the trans isomer was mostly the olefin corresponding to simple elimination[6-8] (eq 1). From



(1)

examination of the probable conformations of the molecules, participation by the transannular hydrogen of the cis isomer in the rate-determining step appeared to be indicated (eq 2). Only the cis isomer has a geometry



(2)

which will permit such participation. The trans isomer reacts without participation, and without much rearrangement. However, the difference in rate between the cis and trans isomers was only a factor of 34, and not large enough to be convincingly attributed to neighboring group participation. Since the *tert*-butyl group is obviously quite bulky, it may well deform appreciably the cyclooctane ring to which it is attached, and hence the earlier experiments did not conclusively rule out the possibility that the unusual rate for the cis isomer was a result of conformational distortion of the ring by the *tert*-butyl group, rather than of neighboring group participation in the usual sense. The rearranged product in that case would have to be formed by a trans-

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