Registry No.—3,4-Epoxycyclopentene, 7129-41-1; 3,4-epoxycyclohexene, 6705-51-7; 3,4-epoxycycloheptene, 6669-45-0; 3,4-epoxycyclooctene, 6690-12-6; 5,6-epoxycyclooctene, 637-90-1; 4,5-epoxy-2,5-dimethyl-2-hexene, 13295-59-5; 3-cyclopentenol, 3212-60-0; 3-cyclohexenol, 822-67-3; 3-cycloheptenol, 4096-38-2; 3-cyclooctenol, 3212-75-7; 4-cyclooctenol, 4114-99-2; 2,5-dimethyl-4-hexen-2-ol, 14908-27-1.

Acknowledgments.—Partial support of this work by the National Science Foundation (GM 6610) and the Public Health Service (GM 12860) is gratefully recorded. Thanks are also due the Columbian Carbon Co. for generous gifts of 1,3- and 1,5-cyclooctadiene.

The Mechanism of Formation of 1-Phenylcyclobutene upon Reaction of 1-Phenyl-1,4-dichloro-1-butene with Magnesium

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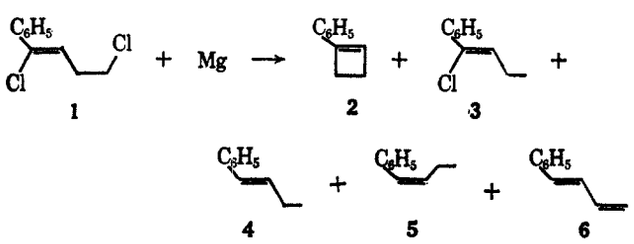
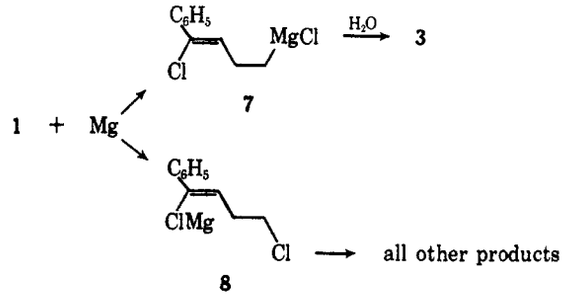
Newman and Kaugars recently reported[1] that 1-phenyl-1,4-dichloro-1-butene (**1**) is converted, upon reaction with magnesium in ether, into a complex mixture containing 1-phenylcyclobutene (**2**), *trans*-1-chloro-1-phenyl-1-butene (**3**), *trans*-1-phenyl-1-butene (**4**), *cis*-1-phenyl-1-butene (**5**), and 1-phenyl-



1,3-butadiene (**6**). In general, the yields of **3**, **4**, and **5** were roughly constant, but the relative yields of **2** and **6** were not reproducible. Some runs gave much **2** and little **6**, while in other, apparently identical, runs, little **2** and much **6** was found. In a given run, the ratio of **2** to **3** and the absolute yields of these did not vary with time. These latter observations led to the conclusion that the primary Grignard reagent **7**, once formed, undergoes no further reaction until hydrolysis, which yields **3**.

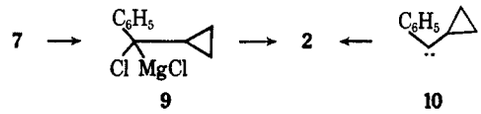
It was therefore concluded that reaction of **1** at the vinylic chloride to form **8** must occur at a rate comparable with reaction at the primary chloride to form **7**. Vinylmagnesium compound **8** was suggested to lead to **2** by an intramolecular nucleophilic substitution, to **4** and **5** by further reaction with magnesium to form a di-Grignard reagent before hydrolysis, and to **6** by either direct intramolecular dehydrohalogenation or by conversion to a dienyl-Grignard reagent, sub-

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



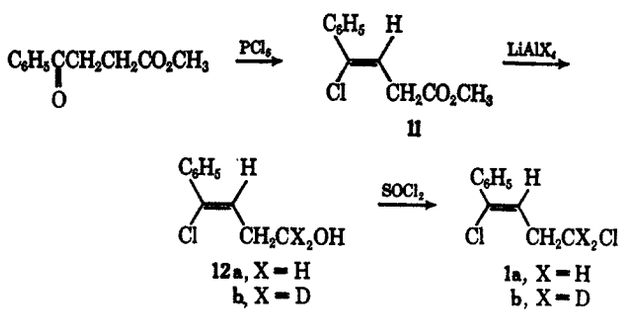
sequently protonated. The lack of reproducibility in the ratio of **2** to **6** could not be accounted for.

The present investigation was initiated because an alternate pathway from **1** to **2** seemed reasonable. Roberts and co-workers[2] have demonstrated the interconversion of the α- and β-carbons of a number of allylcarbinyl Grignard reagents and have suggested cyclopropylcarbinyl Grignard species as plausible intermediates for the interconversions. For example, the nmr spectrum of the Grignard reagent prepared from 4,4-diphenyl-1-bromo-3-butene-1,1-d_2, when taken 5 hr after the start of preparation at 20°, indicated that complete equilibration of the methylene carbons had already taken place.[2] The corresponding allylcarbinyl–cyclopropylcarbinyl interconversion starting from **7** would afford the α-halo Grignard reagent **9**. This, as with other α-halo metallic species,[3] ought to



have much the same chemistry as phenylcyclopropylcarbene (**10**). In fact, the only decomposition pathway of **10** is conversion to 1-phenylcyclobutene **2**[4] and hence the formation of **2** *via* **7** would appear at least as reasonable as *via* **8**. It was decided to investigate this reaction by a deuterium-labeling experiment.

Treatment of benzoylpropionic acid methyl ester with phosphorus pentachloride[5] afforded the chloro



ester **11**, converted by lithium aluminum hydride into **12a** and then with thionyl chloride and tri-*n*-butylamine to **1a**, identical with material prepared by the reaction of phosphorus pentachloride with phenyl cyclopropyl ketone.[6] Reduction of the ester with lithium aluminum deuteride and subsequent reaction with thionyl chloride led to the deuterated analog **1b**.

(2) M. E. H. Howden, A. Maercker, J. Burdon, and J. D. Roberts, *J. Am. Chem. Soc.*, **88**, 1732 (1966), and references therein.

(3) (a) G. L. Closs and R. A. Moss, *ibid.*, **86**, 4042 (1964); (b) M. J. Goldstein and W. R. Dolbier, Jr., *ibid.*, **87**, 2293 (1965).

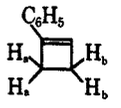
(4) J. A. Smith, Ph.D. Dissertation, Ohio State University, 1964.

(5) T. L. Jacobs, *Org. Reactions*, **5**, 20 (1949).

(6) M. S. Newman and G. Kaugars, *J. Org. Chem.*, **31**, 1379 (1966).

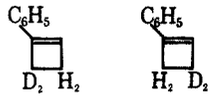
Mass spectrometric analysis of **1b** indicated an isotopic composition of 1.7% d_1, 95.1% d_2, and 3.2% d_3.

The reaction of **1** with magnesium was quite sensitive to the purity of reagents. With ordinary Grignard-quality magnesium turnings, little or no reaction was observed; with singly sublimed magnesium and with **1a** or **1b** which had been purified by preparative vapor phase chromatography (vpc), spontaneous reflux took place when the reactants were mixed in dry ether. When 1-phenylcyclobutene was isolated from the reaction mixture derived from **1a** by preparative vpc, its nmr spectrum consisted of aromatic absorption at about τ 2.9 and multiplets for the vinyl proton at τ 3.9 and for the two methylene groups in **2** at τ 7.3 (H_a) and 7.6 (H_b). Taking advan-



2

tage of the fact that the Newman–Kaugars mechanism would predict only **13** from **1b**, whereas the route through **9** would give an equimolar mixture of **13** and **14**, decomposition of deuterated dichloride **1b** was



13 **14**

carried out. The reported[1] difficulty in reproducing yields of 1-phenylcyclobutene from this reaction was confirmed and it was noted that the deuterium distribution was also subject to variation from run to run (Table I). Since the ratio of H_b to H_a was greater

TABLE I
RELATIVE HYDROGEN DISTRIBUTIONS IN DEUTERATED 1-PHENYLCYCLOBUTENE[a] BY NMR SPECTROSCOPY

Run	H_a	H_b	H_b/H_a	% of reaction *via* **9**	Yield of 1-phenylcyclobutene, %
1	0.85 ± 0.05	1.15 ± 0.06	1.35 ± 0.15	85 ± 5	13 ± 2
2	0.87 ± 0.10	1.13 ± 0.10	1.30 ± 0.27	87 ± 10	10 ± 2
3	0.96 ± 0.04	1.04 ± 0.03	1.08 ± 0.07	96 ± 4	30 ± 3
4	0.89 ± 0.08	1.11 ± 0.10	1.25 ± 0.23	89 ± 8	15 ± 2

[a] Areas under H_a and H_b, normalized to 2; precision of measurement is indicated.

than unity in all runs (although near the limits of experimental precision), the Newman–Kaugars mechanism is probably a minor route to 1-phenylcyclobutene, but the results indicate that the route *via* **9** is predominant.[7,8] The results call for a modified version of the reaction mechanism as first proposed.[1] Grignard reagent **7** was thought[1] to exist unchanged in the mixture until protolyzed to afford **3**. This cannot be true, for conversion of **7** to **2** *via* **9** constitutes an irreversible pathway for destruction of **7** and the ratio of **2** to **3** should increase with time. Since this does not occur,[1] **7** must be converted into **3** *before* protolysis by abstraction of a proton from some other species in the mixture, possibly **1** or **8**.[9]

(7) E. A. Hill and J. D. Roberts [*J. Am. Chem. Soc.*, **89**, 2047 (1967)] have recently made a preliminary report of the conversion of 4-bromo-1-chloro-1-butene-2-4,4-d_2 into an equimolar mixture of cyclobutene-1,3,3-d_3 and cyclobutene-2,3,3-d_3, indicating again exchange of the methylene carbons in a similar reaction.

(8) The conversion of **7** → **9** is thus demonstrated, but the data do not indicate whether or not this reaction is reversible.

Experimental Section[10]

Methyl 3-benzoylpropionate[11] was prepared by the method of Kohler and Engelbrecht.[11] Its nmr spectrum consisted of a multiplet from τ 2.45 to 2.78, a singlet at 6.39, and triplets at 6.84 and 7.39, relative areas 5:3:2:2, respectively.

Methyl 4-Phenyl-4-chloro-3-butenoate (11).—A solution of 12.8 g of methyl 3-benzoylpropionate (0.067 mole) in 25 ml of carbon tetrachloride was added slowly to a refluxing suspension of 25 g (0.12 mole) of phosphorus pentachloride in 50 ml of carbon tetrachloride. After 30 min reflux, 55 ml of the solvent was distilled and the residue was then poured onto ice and extracted with ether. The ether solution was washed with equal portions of water, saturated sodium bicarbonate, saturated sodium chloride, and water. The ether solution was dried over magnesium sulfate and the solvent was removed at the rotary evaporator. Methyl 4-phenyl-4-chloro-3-butenoate (**11**) was distilled under reduced pressure, bp 100° (0.2 mm). The nmr spectrum of **11** consisted of a multiplet from τ 2.4 to 2.9, a triplet at 3.76 (J = 6.5 cps), a singlet at 6.43, and a doublet at 6.72 (J = 6.5 cps), relative areas 5:1:3:2, respectively. These are assigned in turn to the aromatic, vinyl, methyl, and methylene protons of **11**.

Anal. Calcd for $C_{11}H_{11}O_2Cl$: C, 62.72; H, 5.26; Cl, 16.83. Found: C, 62.53; H, 5.25; Cl, 17.07.

1-Phenyl-1,4-dichloro-1-butene (1a).—To a chilled solution of 2.00 g (0.011 mole) of **11** in 10 ml of anhydrous ether was added a suspension of lithium aluminum hydride, 0.44 g (0.012 mole) in 20 ml of ether. The mixture was allowed to warm to room temperature over a 1-hr interval. Water (1 ml) was added dropwise, the inorganic salts were removed by filtration, and the filtrate was dried over magnesium sulfate. Distillation of the ether afforded crude **12a**, whose infrared spectrum indicated hydroxyl absorption at 2.98 μ and the absence of the carbonyl absorption of **11** at 5.72 μ.

To a solution of 1.00 g of the alcohol (0.0055 mole) in 10 ml of anhydrous ether at 0° was added tri-*n*-butylamine, 1.01 g (0.0055 mole). A solution of 0.65 g of thionyl chloride (0.0055 mole) in 20 ml of ether was added dropwise with stirring. The mixture was allowed to warm to room temperature over a 2-hr interval. Cold water was added and the ether phase was separated, washed with three 25-ml portions of water, and dried over magnesium sulfate. After ether was removed at the rotary evaporator, the chloride was chromatographed over silica gel (elution with 5% ether in pentane) and finally purified by preparative vpc. Its nmr spectrum was identical with that of a sample prepared by another route.[6]

1-Phenyl-4,4-dideuterio-1,4-dichloro-1-butene (1b).—Substitution of lithium aluminum deuteride in the above scheme afforded the deuterated dichloride **1b**. Its nmr spectrum was identical with **1a**, except that the two-proton triplet at τ 6.60 ($-CH_2Cl$) in **1a** was absent. Mass spectrometry (Morgan–Schaffer Corp., Montreal, Canada) indicated an isotopic distribution of 1.66% d_1, 95.12% d_2, and 3.22% d_3.

The reactions of **1a** and **1b** with magnesium were carried out by the procedure of Newman and Kaugars (expt 9 in their Table I).[1] The 1-phenylcyclobutene was separated by preparative vpc and analyzed by nmr spectroscopy as indicated in the discussion (see Table I).

Registry No.—**1a**, 5680-48-8; **1b**, 14908-29-3; **2**, 3365-26-2; magnesium, 7439-95-4; **11**, 14908-31-7; **12a**, 14908-32-8.

Acknowledgment.—Financial support of this research by the Petroleum Research Fund of the American Chemical Society is gratefully acknowledged.

(9) The formation of **3** might also involve a free-radical mechanism;[2] we have no data compelling or ruling out this reaction course.

(10) Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. All nmr spectra were measured in carbon tetrachloride on a Varian A-60A spectrometer, relative to external tetramethylsilane. Analytical and preparative vpc separations were carried out using a Varian Aerograph Model 90-P3 chromatograph on a 2-ft column packed with 10% SE-30 on Fluoropak 80.

(11) E. P. Kohler and H. Engelbrecht, *J. Am. Chem. Soc.*, **41**, 764 (1919).