TABLE I

REACTIONS OF 2,2,2-TRIFLUOROETHYL THIOLACETATE WITH PIPERIDINE (30°, μ = 1.0, in H_2O)

pH	$a_H \times 10^{12}$ M	$[OH^-] \times 10^4$ M	$K_a'/(K_a' + a_H)$	k_I, min^{-1}	k_2', M^{-1} min^{-1}	Buffer concn range, M	No. of k_{obsd}
10.20	63.10	5.1	0.1118	0.15	85	0.002–0.4	12
10.63	23.44	6.55	0.2531	0.2	203	0.002–0.4	11
11.15	7.08	20.76	0.5288	0.30	445	0.002–0.05	12
11.50	3.16	46.48	0.7150	0.6	575	0.002–0.3	8
11.80	1.59	92.74	0.8337	1.0	720	0.001–0.25	8

case 3, we noted that fallacious results were being obtained from the stopped-flow apparatus then in use. This finding has led us to reinvestigate case 3.[7]

Our studies of the reaction of 2,2,2-trifluoroethyl thiolacetate with piperidine buffers at different pH's have produced results remarkably different from those observed by Gregory and Bruice.[1] The reactions were studied at five different pH's (in the range 10.20–11.80). At each pH, 8–12 buffer concentrations covering mostly a 200–250-fold dilution were studied. The results are shown in Table I. It was found that even over a 250-fold change in total buffer concentration, the reaction was first order in the ester concentration and first order in the total buffer concentration. Plots of k_{obsd} *vs.* $[B_T]$ (shown in Figure 1) were linear over the whole concentration range at all pH's with slopes = k_2' and intercept = k_I, where k_2' is the apparent second-order rate constant at a given pH. Plots of k_2' *vs.* $K_a'/(K_a' + a_H)$ (Figure 2) were linear of slope = k_2 (8.33×10^2 l. mole^{-1} min^{-1}) and intercept zero, where k_2 is the true second-order rate constant. Similarly, a plot of k_I *vs.* $[OH^-]$ (Figure 3) yielded a straight line with a slope of k_{OH} = 95 l. mole^{-1} min^{-1}. The reactions can, hence, be expressed by eq 4. A

$$\frac{-d[E]}{dt} = (k_I + k_2'[B_T])[E] = (k_0 + k_{OH}[OH^-] + k_2\frac{K_a'}{(K_a' + a_H)}[B_T])[E] \quad (4)$$

comparison of the k_{OH} value (95 l. mole^{-1} min^{-1}) obtained from our studies with the k_{OH} (64.5 l. mole^{-1} min^{-1}) obtained by Gregory and Bruice[1] with the aid of a pH Stat shows that they are in good agreement. This rules out the possibility of any piperidine catalysis of water addition to the ester. It can be concluded, therefore, that the reaction of 2,2,2-trifluoroethyl thiolacetate in piperidine buffers follows the reaction pattern observed in the reactions of other nucleophiles with this substrate; *i.e.*, a slower attack by the nucleophile at the carbonyl carbon is followed by a faster collapse of the intermediate. The reaction of piperidine with 2,2,2-trifluoroethyl thiolacetate is similar to its reaction with *p*-nitrophenyl acetate[8] ($k_2 = 8.33 \times 10^2$ l. mole^{-1} min^{-1} for the former case compared to $k_2 = 9.33 \times 10^2$ l. mole^{-1} min^{-1} for the latter). This is predictable on the basis of the similar pK_a' values of 2,2,2-trifluoroethanethiol (7.3) and *p*-nitrophenol (7.15).

Thus, the second-order reaction of piperidine with 2,2,2-trifluoroethyl thiolacetate (k_S) and *p*-nitrophenyl acetate ($k_{p\text{-NPA}}$) follow the relationship given by eq 5

$$\log k_{p\text{-NPA}} = \log k_S + 0.6 \quad (5)$$

which has been established for the reaction of 12 other nucleophiles with these substrates.[1]

Registry No.—Piperidine, 110-89-4; 2,2,2-trifluoroethyl thiolacetate, 14897-48-4.

Acknowledgment.—This work was supported by a grant from the National Institutes of Health.

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[7] Experimental procedures are those reported in ref 1. The stopped-flow apparatus employed in this study was the 13001 Durrum-Gibson model with a Kel-F cell and valve block (T = 30°, μ = 1.0 with KCl).

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A Synthesis of Homoallylic Alcohols

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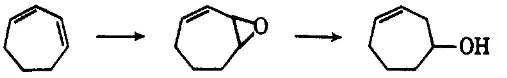
During the course of studies concerned with developing the chemistry of monoepoxides of conjugated dienes,[2] we have found that these materials serve as useful intermediates in a selective, efficient conversion of certain conjugated dienes into homoallyic alcohols, as exemplified by eq 1.



(1)

The process involves peracetic acid oxidation of the diene, followed by lithium aluminum hydride reduction of the resulting epoxide. Both of these reactions have been utilized on occasion in the literature,[3] but a major drawback has been the difficulty associated with obtaining the sensitive epoxides. Application of the elegant procedure developed by Korach and coworkers[4,5] for the preparation of the exceedingly reactive cyclopentadiene monoepoxide allows this difficulty to be circumvented. The oxidation method consists of a slow addition of commercial 40% peracetic acid (in acetic acid) to an ice-cold, stirred solution of the diene in methylene chloride containing suspended sodium carbonate. The sodium carbonate functions as a buffering agent by removing acetic acid from the reaction solution. Although the original procedure used an excess of the diene, the present studies demonstrate that good yields of monoepoxides can be obtained with a 1:1 ratio of reactants. This observation indicates that the monoepoxide reacts

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[1] (a) National Science Foundation Undergraduate Research Participant; (b) National Defense Education Act Title IV Predoctoral Fellow.

[2] J. K. Crandall and R. J. Watkins, *Tetrahedron Letters*, 1717 (1967).

[3] A. C. Cope and P. E. Peterson, *J. Am. Chem. Soc.*, **81**, 1643 (1959); J. G. Traynham and P. M. Greene, *ibid.*, **86**, 2657 (1964).

[4] M. Korach, D. R. Nielsen, and W. H. Rideout, *ibid.*, **82**, 4328 (1960).

[5] Several of the compounds prepared in this study have also been obtained in a similar fashion by N. Heap and G. H. Whitham [*J. Chem. Soc.*, *Sect. B*, 164 (1966)], although the details of this work are rather sparse.

substantially slower with peracid than does the diene and allows for a simplification of the purification method, since large quantities of diene need not be separated from the desired product. Since epoxidation is very sensitive to electronic and steric effects of substituents,[6] it is likely that a high degree of selectivity can be realized in the functionalization of unsymmetrical dienes, although this particular point has not thus far been demonstrated.

The lithium aluminum hydride reduction is also very selective in promoting hydride attack at the allylic carbon. In none of the present examples has the corresponding allylic alcohol been found, although in several instances as little as 1-2% would have been easily detected. However, butadiene monoepoxide yields substantial quantities of the allyl alcohol,[7] which suggests that terminal diene epoxides will not show the selectivity associated with the present examples.

The cyclic conjugated dienes from C_5 to C_8 give purified epoxides in yields of 45–78% and are reduced to alcohols in yields of 78–88%. Noteworthy is the preparation of 3-cyclopentenol, which is superior to previous methods of synthesis[8] for this compound. The same procedure is useful in converting 1,5-cyclooctadiene, a nonconjugated diene, into 4-cyclooctenol by way of its reactive monoepoxide. Finally, 2,5-dimethyl-2,4-hexadiene was used to obtain the open-chain homoallylic alcohol, 2,5-dimethyl-4-hexen-2-ol.

Experimental Section

General.—Infrared spectra were obtained with Perkin-Elmer 137 and 137G Infracord spectrophotometers and nuclear magnetic resonance spectra with a Varian A60 spectrometer (carbon tetrachloride solutions). Gas chromatography was performed on Aerograph 600 (analytical, flame ionization detector) and A700 (preparative) instruments. Microanalyses were performed by the Midwest Microlabs, Inc.

Epoxidation Procedure. 3,4-Epoxycyclopentene.[4]—To an ice-cold, mechanically stirred mixture of 45 g (0.68 mole) of freshly cracked cyclopentadiene and 290 g of powdered, anhydrous sodium carbonate in 750 ml of methylene chloride was added dropwise 126 g (0.67 mole) of 40% peracetic acid which had been pretreated with a small amount of sodium acetate. The mixture was stirred at room temperature until a negative test was obtained with moist starch–iodide paper. The solid salts were removed by suction filtration and washed well with additional solvent. The solvent was removed from the filtrate by distillation through a Vigreux column and the residue was distilled into an ice-cold receiver to give 25 g (45%) of 3,4-epoxycyclopentene, bp 39–41° (46 mm). The infrared spectrum has bands at 3.3, 5.95 (w), 11, 12.1, and 12.3 μ. The nmr spectrum displays two-proton complex multiplets at τ 4.0, 6.3, and 7.6.

In a similar fashion, the following epoxides were prepared.

3,4-Epoxycyclohexene.[9]—Cyclohexadiene (17 g) was converted into 14 g (69%) of epoxide: bp 62–64° (65 mm); infrared, 3.3, 6.1, 10.8, 11.6, 12.4, and 12.7 μ; nmr, complex multiplets at τ 4.2 (2 H), 6.7 (1 H), 6.95 (1 H), and 7.5–8.7 (4 H).

3,4-Epoxycycloheptene.[5]—Cycloheptadiene (20 g) was converted into 11.8 g (50%) of epoxide after spinning-band distillation: bp 90–96° (76 mm); infrared, 6.0, 10.5, 10.75, 11.35, 12.4, and 13.7 μ; nmr, complex multiplets at τ 4.2 (2 H), 7.9 (4 H), 8.4 (2 H), and an almost symmetrical multiplet (2 H) centered at 6.9.

Anal. Calcd for $C_7H_{10}O$: C, 76.33; H, 9.15. Found: C, 76.45; H, 9.25.

3,4-Epoxycyclooctene.[3,5]—1,3-Cyclooctadiene (200 g) was converted into 180 g (78%) of epoxide after spinning-band distillation: bp 94–97° (41 mm); infrared, 6.1, 9.7, 9.9, 10.6, 11.8, 12.3, and 13.8 μ; nmr, multiplets at τ 4.4 (2 H), 6.75 (1 H), 7.05 (1 H), and 7.5–9.0 (8 H).

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.43; H, 9.63.

5,6-Epoxycyclooctene.[3,5]—1,5-Cyclooctadiene (145 g) was converted into 80 g (48%) of epoxide after spinning-band distillation: bp 98–100° (37 mm); infrared, 6.1, 9.7, 10.7, 11.6, 13.1, 13.4, and 14.4 μ; nmr complex multiplets at τ 4.45 (2 H), 7.15 (2 H), and 7.5–8.3 (8 H).

Anal. Calcd for $C_8H_{12}O$: C, 77.38; H, 9.74. Found: C, 77.64; H, 9.68.

4,5-Epoxy-2,5-dimethyl-2-hexene.[10,11]—2,5-Dimethyl-2,4-hexadiene (20 g) was converted into 6.8 g (30%) of epoxide: bp 70–71° (38 mm); mp 58–60° (after sublimation); infrared, 6.0, 7.30, 9.0, 11.5, 11.9, and 12.5 μ. The nmr data agreed with that published.[10] Even the buffered oxidation method gave large quantities of unidentified higher boiling rearrangement products whose infrared spectrum indicates the presence of both carbonyl and hydroxyl.

Reduction Procedure. 3-Cyclopentenol.[8]—3,4-Epoxycyclopentene (10.0 g, 0.12 mole) was added dropwise to an ice-cold, stirred slurry of 2.55 g (0.07 mole) of lithium aluminum hydride in 250 ml of anhydrous ether. After 3 hr the reaction was quenched by the dropwise addition of 10 ml of water. Anhydrous magnesium sulfate was added to the mixture and after stirring a few minutes the inorganic salts were removed by suction filtration and washed well with additional solvent. The solvent was removed from the filtrate by distillation through a Vigreux column and the residue was distilled to yield 8.8 g (88%) of 3-cyclopentenol: bp 71–73° (46 mm); infrared spectrum, 3.0, 3.3, 6.2, 9.5, 10.5, and 12 μ; nmr, τ 4.38 (broad singlet, 2 H), 5.59 (seven-line symmetrical signal, 1 H), 6.0 (1 H), and 7.1–8.0 (4 H).

Material of comparable purity can be obtained by reduction of the crude epoxidation product without further purification and spinning-band distillation of the crude alcohol.

In a similar fashion the following alcohols were prepared.

3-Cyclohexenol.[12]—Reduction of 6.0 g of epoxide yielded 4.8 g (78%) of alcohol: infrared, 3.0, 3.3, 6.1, 9.3, 9.5, and 13.6 μ; nmr, τ 4.6 (broad singlet 2 H), 5.4 (1 H), 6.3 (1 H), and 7.6–8.7 (6 H).

3-Cycloheptenol.[13]—Reduction of 8.6 g of epoxide gave 8.0 g (91%) of crude product of greater than 90% purity: infrared, 3.0, 3.3, 6.05, 9.7, and 14.5 μ; nmr, τ 4.3 (2 H), 5.4 (1 H), 6.5 (1 H), and 7.5–8.8 (8 H).

3-Cyclooctenol.[3,5]—3,4-Epoxycyclooctene (62 g) was converted into 51 g (81%) of 3-cyclooctenol: bp 108–112° (20 mm); infrared, 3.0, 6.1, 9.6, 10.8, 12.2, 12.9, 13.2, and 14.2 μ; nmr, τ 4.4 (m, 2 H), 5.8 (1 H), 6.35 (m, 1 H), and complex absorption centered at 7.8 and 8.5 (10 H). This material has also been prepared in good yield from crude epoxide.

4-Cyclooctenol.[3,5]—5,6-Epoxycyclooctene (90 g) was reduced as described above except that the reaction mixture was heated to reflux for 1 day before work-up. The yield of 4-cyclooctenol was 76 g (83%): bp 101–105° (10 mm); infrared, 3.0, 3.3, 6.1, 9.5, 10.1, and 13.8 μ; nmr, τ 4.45 (m, 2 H), 6.0 (1 H), 6.4 (m, 1 H), and 7.6–9.0 (m, 10 H).

2,5-Dimethyl-4-hexen-2-ol.[14]—Reduction of 2.0 g of epoxide gave 1.7 g (82%) of alcohol: bp 74–75° (53 mm); infrared, 3.0, 6.0, 7.28, 8.7, 11.0, 11.7, and 12.8 μ; nmr, τ 4.79 (1 H, triplet of multiplets, $J = 7$, 1.5 cps), 6.8 (1 H), 7.89 (1 H, broad doublet, $J = 7$ cps), 8.35 (6 H, broad doublet, $J = 7$ cps), and 8.86 (6 H, s).

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(6) A thorough review of this subject is available in A. Rosowsky, "Heterocyclic Compounds with Three- and Four-Membered Rings," Part 1, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1964, pp 1–523.

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(9) M. Tiffeneau and B. Tchoubar, *Compt. Rend.*, **212**, 581 (1941).

(10) A. C. Day and M. C. Whiting, *J. Chem. Soc.*, *Sect. C*, 1719 (1966).

(11) With very reactive dienes, it is important to use relatively dilute solutions of the diene to avoid diepoxide formation.

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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.

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

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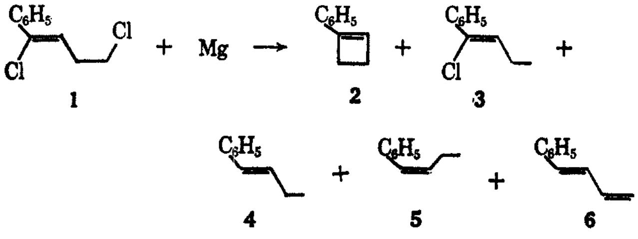
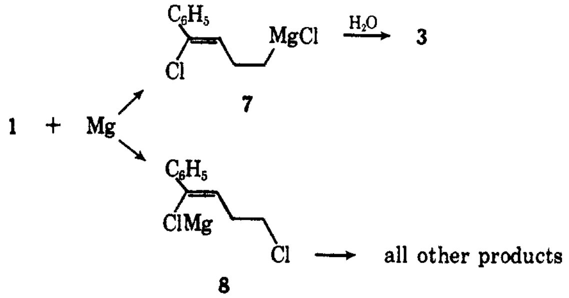
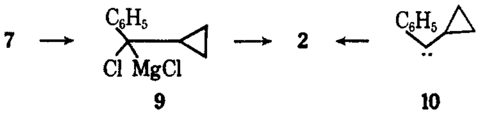
Newman and Kaugars recently reported[1] that 1-phenyl-1,4-dichloro-1-butene (**1**) is converted, upon reaction with magnesium in ether, into a complex mixture containing 1-phenylcyclobutene (**2**), *trans*-1-chloro-1-phenyl-1-butene (**3**), *trans*-1-phenyl-1-butene (**4**), *cis*-1-phenyl-1-butene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



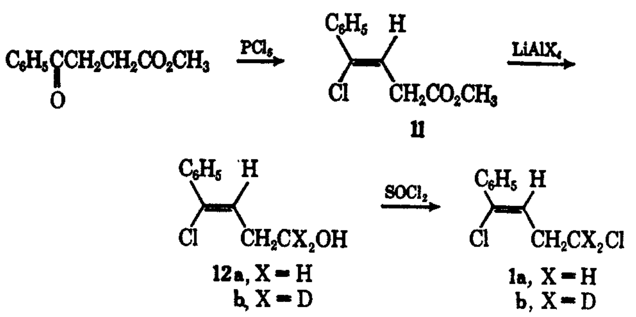
It was therefore concluded that reaction of **1** at the vinylic chloride to form **8** must occur at a rate comparable with reaction at the primary chloride to form **7**. Vinylmagnesium compound **8** was suggested to lead to **2** by an intramolecular nucleophilic substitution, to **4** and **5** 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, subsequently 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**.



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