predict the changes in the transition state geometry. However, it has been recently suggested that perpendicular effects should prevail for "reactant-like" or "product-like" transition states whereas parallel effects should predominate when the transition state is "carbanion-like" or "carbocation-like".[7c]

In going from associated to dissociated *t*-BuOK there is a significant increase[8] in medium basicity and this structural change should favor both the product and the carbanion.[7b] Therefore, both parallel and perpendicular effects may play a role in determining the sensitivity of the transition state structure to changes in medium basicity. On this basis, the different behaviors of the reactions of 2-arylethyl bromides and 1-chloro-1-phenyl-2-arylethanes could be tentatively explained by suggesting a more "reactant-like" transition state for the latter reaction, owing to the much larger stability of the formed olefin,[9] and, consequently, a greater importance of the perpendicular effects. Thus, an increase in the medium basicity could increase the carbanion character of the transition state in the case of the eliminations from 1-chloro-1-phenyl-2-arylethanes and have practically no effect in the case of the eliminations from 2-arylethyl bromides.

Whatever the correct explanation, the present results clearly support the suggestion[7c,d] that the sensitivity of the transition state of an E2 reaction to structural changes can depend on the character of the transition state itself and its position in More O'Ferrall's potential energy diagram.[7b] It appears therefore particularly dangerous to draw general conclusions concerning this problem from the results of only one series of substrates.

The comparison of the data reported here with the corresponding ones relative to the reaction of 2-phenylethyl chloride[1] allow us to evaluate the kinetic effect of an α-phenyl group in these eliminations. It is interesting to note that the introduction of an α-phenyl group produces a significant rate-retarding effect (ca. two-fold, after consideration of the statistical factor[10]) in the reaction promoted by complexed *t*-BuOK, whereas no kinetic effect is found in the reaction carried out in the presence of crown ether. These findings compare with the six-fold accelerating effect observed (at 50°C) in the eliminations promoted by EtONa in EtOH.[11]

Experimental Section

Materials. **1-Chloro-1-phenyl-2-arylethanes** were available from a previous study.[11]

18-Crown-6 ether (18C6) was a commercial product (Fluka) purified by crystallization from *n*-hexane, mp 38.5–39.5 °C (lit.[12] mp 39.5–40.5 °C).

Base–Solvent Solution. *tert*-Butyl alcohol was distilled after treatment with potassium metal. Solution of alkoxide was obtained by reaction, under nitrogen, of freshly cut potassium with *tert*-butyl alcohol.

Kinetic Studies. For all compounds but 1-chloro-1-phenyl-2-*p*-nitrophenylethane, kinetics were carried out in a stoppered two-limb silica cell, either in the presence or in the absence of 18C6. In one limb was placed the substrate solution (1 mL) and in the other the base solution (1 mL). The cell was placed in the thermostated compartment of a Beckman DB-GT spectrophotometer. After ca. 0.5 h the solutions were mixed thoroughly and the cell was rapidly placed again in the compartment of the spectrophotometer. Absorbances were measured at the following wavelengths (nm): 298 for *trans*-stilbene; 299 for *p*-chloro-*trans*-stilbene; 298 for *p*-methyl-*trans*-stilbene; and 348 for *p*-nitro-*trans*-stilbene.

In the experiments with complexed base the reference cell contained a solution of potassium *tert*-butoxide and 18C6 in *tert*-butyl alcohol at the same concentration used in the kinetic run, to compensate for the significant absorption by complexed *t*-BuOK. At the wavelengths used for measurements in this study, the compensation was effective in the range 0.01–0.1 M of *t*-BuOK–18C6 concentration.

The elimination from 1-chloro-1-phenyl-2-*p*-nitrophenylethane, in the presence of 18C6, was followed on a Durrum-Gibson D-110 stopped-flow spectrophotometer.

The yield of olefin was determined from the value of D_∞ (optical density at infinite time) and pseudo-first-order rate constants were determined from the slope of a plot of log $(D_\infty - D_t)$ against time. Second-order rate constants, k_2, were obtained by dividing the first-order rate constants by the base concentration.

Acknowledgment. This work was carried out with the financial support of the Italian National Research Council (C.N.R.).

Registry No.—*trans*-Stilbene, 103-30-0; *p*-chloro-*trans*-stilbene, 1657-50-7; *p*-methyl-*trans*-stilbene, 1860-17-9; *p*-nitro-*trans*-stilbene, 1694-20-8; 18-crown-6 ether, 17455-13-9.

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(9) The fact the two reactions have similar ρ values in *t*-BuOK–*t*-BuOH does not necessarily imply a similar location of the transition state in the potential energy surface, owing to the quite significant structural differences between the two reaction series.
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Acceleration of an Allylic Rearrangement by the Cyclopropyl Substituent. Reaction Conditions to Prevent Ring Opening[1]

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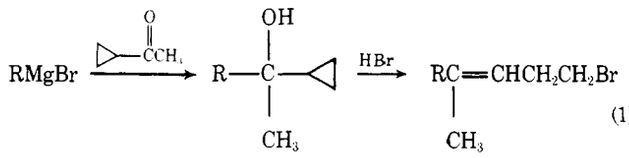
Although it is well known[2] that the cyclopropyl group has a remarkable ability to stabilize an α positive charge, there are conflicting data in the chemical literature as to whether the cyclopropyl or phenyl substituent is better able to delocalize a positive charge on an adjacent carbon. For example, it has been reported[3] that methyl cyclopropyl ketone is more basic than methyl isopropyl ketone and significantly more basic than acetophenone in H_2SO_4–H_2O or CF_3CO_2H–H_2SO_4 solutions, indicating that the cyclopropyl group is better able to delocalize an adjacent positive charge than is a phenyl group. On the other hand, Olah and White have demonstrated[4] that a phenyl group is considerably more effective than cyclopropyl in stabilizing an α carbonium ion by measuring the ^{13}C NMR chemical shifts of the sp^2 carbon in related cyclopropyl- and phenyl-substituted carbonium ions. This note discusses a series of experiments involving the acid-catalyzed rearrangement of tertiary vinyl carbinols (**2**) in acetic acid that not only demonstrates the remarkable ability of the cyclopropyl substituent to stabilize an adjacent cationic center but also provides some evidence concerning the nature of the reaction intermediate vs. the question of cyclopropane ring opening.

The acid-catalyzed ring opening of cyclopropanoids is a well-known reaction. For example, the Julia synthesis[5] of homoallylic halides is dependent on such cyclopropyl ring cleavage (eq 1). However, as Breslow has noted in his review of rearrangements of small ring compounds,[6] it is possible for

Table I. Allylic Rearrangement[a] of Tertiary Vinyl Carbinol 2a

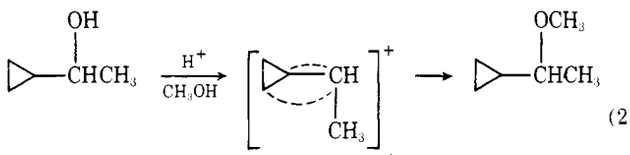
Entry	Solvent	Ratio[b] of 3a:3b:4c:4b:2a	Distilled yield, %	% yield[c] of tosylate 4d
1	Glacial HOAc[d]	25:1:1:0:0	68	8
2	Glacial HOAc	10:1.2:1:0:0	59	7
3	25:1 (v/v) HOAc–H_2O[e]	6:1:1:0:1	75	2
4	10:1 (v/v) HOAc–Ac_2O	8.3:3.3:1:0:0	68	8
5	Glacial HOAc containing sodium tosylate[f] (0.2 M solution)	56:40:3:1:0	64	8
6	Glacial HOAc[g]	1:0:20:0:0	12	17

[a] All reactions, unless indicated otherwise, were run for 30 s at 15 °C using *p*-toluenesulfonic acid (0.0125 M solution) as the catalyst, the solution being 0.1 M with respect to alcohol **2a.** [b] In the distilled product. Determined by NMR and VPC analysis. No other compounds could be detected in the distilled product. With longer reaction times (i.e., 1 or 2 min), the amount of alcohol **3a** diminished by its conversion to the corresponding acetate **3b.** The amount of ring-opened products remained constant, however. [c] Tosylate **4d** was isolated by chromatography of the distillation residue on silica gel (elution with hexane–8% ether). [d] The concentrations of alcohol **2a** and the catalyst were 0.02 and 0.0025 M, respectively, for this reaction. [e] This reaction was run for 60 s at 15 °C and evidently proceeded at a much slower rate, as indicated by the presence of approximately 10% starting material (**2a**) in the product mixture. [f] Prepared in situ by treatment of tosic acid with 1 equiv of anhydrous sodium acetate. [g] The concentration of *p*-toluenesulfonic acid was 0.50 M for this reaction.



(1)

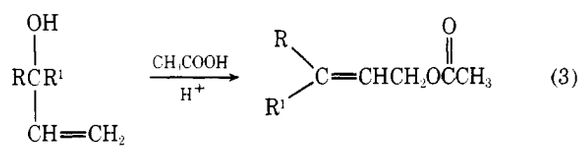
substituted cyclopropylcarbinyl derivatives to show very high reactivity and yet yield unrearranged derivatives. For example, the reaction[7] depicted in eq 2 proceeds quite rapidly and



(2)

is presumed to occur via protonation of the hydroxyl substituent followed by loss of water to form a nonclassical bicyclobutonium ion, which is subsequently attacked by the solvent at the center of maximum charge.

We decided to investigate the solvolysis of 2-cyclopropyl-3-buten-2-ol (**2a**) in acetic acid containing a strong acid catalyst. The latter conditions have recently been shown[8] to be useful for the rearrangement of tertiary vinyl carbinols to the corresponding primary allylic acetates (eq 3). Indeed, treat-

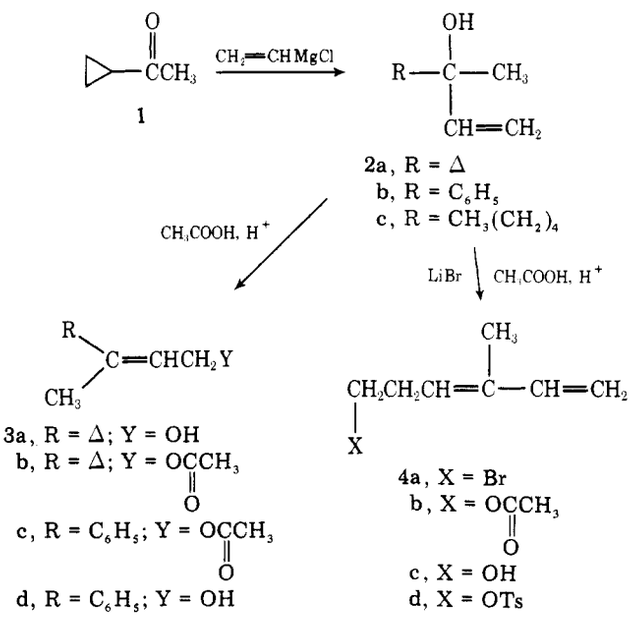


(3)

ment of alcohol **2a** (0.02 M solution) with glacial acetic acid containing *p*-toluenesulfonic acid (0.0025 M) at 15 °C for 30 s led to its facile rearrangement, without any appreciable ring opening,[9] to a 25:1 mixture of the corresponding primary allylic alcohol (**3a**) and its acetate derivative (**3b**) in 68% yield after evaporative distillation. The formation of alcohol **3a** as the major product[10] is remarkable in view of the nature of the solvent system and indicates that the reaction intermediate may be an intimate ion pair[11] which undergoes rapid rearrangement to afford the observed products. Such a hypothesis is also consistent with the structure of the only identifiable—and major—component of the nonvolatile portion of the reaction product. This latter substance was isolated in 8% yield by column chromatography on silica gel and identified as ring-opened tosylate **4d.**

The dramatic accelerating effect supplied by the cyclopropyl group in this allylic rearrangement was demonstrated

Scheme I



by running the reaction with 2-phenyl-3-buten-2-ol (**2b**)[8] under identical conditions. The product mixture in this latter reaction was determined by NMR analysis[12] to consist of a 16:1 mixture of unreacted starting material (**2b**) and the expected rearrangement product, 3-phenyl-2-buten-1-ol acetate (**3c**)[8] uncontaminated by any of the corresponding primary allylic alcohol (**3d**). Furthermore, using these same reaction conditions, 3-methyl-1-octen-3-ol (**2c**)[8] was recovered in almost quantitative yield.

Since the minor amount of products derived from cyclopropane ring opening is in direct contrast to an earlier report[13] that the same alcohol (**2a**) when treated with hydrobromic acid reacts with total ring cleavage to afford 6-bromo-3-methyl-1,3-hexadiene (**4a**) in 85% yield, a number of additional experiments were performed using different reaction conditions as outlined in Table I. In none of these reactions were significant amounts of other components detected in the *distilled* product.[14] The necessity of a catalyst was demonstrated by the observation that the starting tertiary vinyl carbinol (**2a**) could be recovered virtually unchanged from 10:1 (v/v) acetic acid–acetic anhydride after a period of 2 min.

Since the addition of lithium perchlorate or lithium bromide is known[11] to change the nature of the intermediate ion pair

in solvolyses by trapping the solvent-separated ion pair to give the unstable $R^+//Br^-$ (or ClO_4^-), two additional reactions were run using these salts as added reagents. In both cases NMR analysis of the reaction product indicated total cleavage of the cyclopropane ring. Using 5:1 (v/v) acetic acid–acetic anhydride as the solvent containing *p*-toluenesulfonic acid (0.025 M solution) and lithium bromide[15] (1 M solution), 2-cyclopropyl-3-buten-2-ol (**2a**) was converted[16] in 75% yield to 6-bromo-3-methyl-1,3-hexadiene (**4a**) as the only detectable reaction product.

An additional experiment (Table I, entry 6) involved treatment of alcohol **2a** (0.1 M solution) with glacial acetic acid containing a substantial amount of *p*-toluenesulfonic acid (0.50 M solution) at 15 °C for 30 s. In contrast to a similar experiment conducted in the presence of a large amount of sodium tosylate (Table I, entry 5), the major identifiable reaction product was ring opened tosylate **4d**, obtained in 17% yield after chromatography[17] on silica gel (elution with hexane–8% ether). Such results, together with an earlier study[13] of the same system (**2a**) using hydrobromic acid, seem to indicate that the presence of the lithium cation or a strong proton donor such as *p*-toluenesulfonic acid disrupts the intimate ion pair (R^+, ^-OTs, H_2O in a solvent cage) leading to cyclopropane ring opening.

Experimental Section[18]

2-Cyclopropyl-3-buten-2-ol (2a). A solution of 5.74 g (68 mmol) of ketone 1[19] in 50 mL of anhydrous ether was added dropwise over a period of 10 min to 40 mL of 2.3 M vinylmagnesium chloride–tetrahydrofuran solution,[20] cooled to 0 °C in an ice water bath and maintained under a nitrogen atmosphere. After this mixture had been stirred at 0 °C for 10 min, the reaction was quenched by dropwise addition of saturated aqueous NH_4Cl solution. Extraction[18] of the product with ether, followed by short-path distillation, afforded 6.27 g (82%) of tertiary vinyl carbinol **2a:** bp 58–60 °C (35 mm) [lit.[21] bp 137 °C (760 mm)]; ν_{max} (film) 3450 (OH), 3100, 1645 (C=C), 1170, 1115, 1050, 1020, 1000, 920 cm^{-1}; δ_{Me_4Si} (CCl_4) 5.82 (CH=CH_2, J_{AC} = 10, J_{BC} = 18 Hz), 5.31–4.83 (CH=CH_2, rest of ABC pattern[22]), 2.08 (s, OH), 1.23 (s, CH_3), 0.87 (multiplet, 1 cyclopropyl H, peaks at 1.03, 0.94, 0.92, 0.80, and 0.71), 0.36 and 0.25 ppm (4 cyclopropyl Hs).

Allylic Rearrangement of Tertiary Vinyl Carbinol 2a. A solution of 228 mg (2.03 mmol) of alcohol **2a** in 2.0 mL of glacial acetic acid was added rapidly to a well-stirred solution of 47 mg (0.25 mmol) of *p*-toluenesulfonic acid monohydrate in 18.0 mL of glacial acetic acid in a stoppered flask kept in a constant temperature bath at 15 °C. After 30 s, the reaction was quenched by quickly pouring the solution into a mixture of 100 mL of 4 N aqueous NaOH and 75 g of crushed ice. Extraction[18] of the product with ether, followed by evaporative distillation, afforded 136 mg (59% corrected yield) of colorless oil, bp 35–55 °C (bath temperature, 0.10 mm). VPC analysis[23] (oven temperature 155 °C, flow 15 mL/min) indicated that the product consisted almost exclusively of a mixture of three components: primary allylic acetate **3b** (retention time 7.6 min, 9.8% of the mixture), the corresponding alcohol **3a** (retention time 4.5 min, 82%), and homoallylic alcohol **4c**[24] (retention time 4.1 min, 8%). Only a trace (<0.3%) of ring-opened acetate (**4b**) (retention time 6.7 min) was detected in the product.[25]

An analytical sample of primary allylic acetate **3b** was obtained by chromatography on silica gel of the distilled product obtained using the conditions cited in Table I, entry 4. Elution with hexane–2% ether afforded the rearranged acetate **3b** as a mixture of *E*:*Z* stereoisomers: bp 77–94 °C (bath temperature, 2.0 mm); ν_{max} (film) 1745 (C=O), 1665 (C=C), 1240, 1025, 950 cm^{-1}; δ_{Me_4Si} (CCl_4) 5.31 (broad triplet, J = 7 Hz, C=CH), 4.48 (doublet, J = 7 Hz, CH_2OAc), 1.97 [s, OC(=O)CH_3], 1.60 (s, vinyl CH_3), ~80% of the mixture), 1.48 (s, vinyl CH_3, ~20% of the mixture), 1.3 (complex multiplet, 1 cyclopropyl H), 0.55 ppm (complex multiplet, 4 cyclopropyl Hs). Anal. Calcd for $C_9H_{14}O_2$: C, 70.04; H, 9.16. Found: C, 70.01; H, 9.17.

An authentic sample of the corresponding primary allylic alcohol (**3a**) was obtained by chromatography of the distilled product obtained using the conditions cited in Table I, entry 1. Elution with hexane–20% ether afforded alcohol **3a:** bp 70–85 °C (bath temperature, 2.0 mm) [lit.[26] bp 88 °C (13 mm)]; ν_{max} (film) 3350 (OH), 1665 (C=C), 1085, 1045, 1000, 955, 895, 815 cm^{-1}; δ_{Me_4Si} (CCl_4) 5.36 (triplet, J = 7 Hz, C=CH), 4.02 (doublet, J = 7 Hz, CH_2OH), 3.67 (s, OH), 1.56 (s, vinyl CH_3, ~80% of the mixture), 1.44 (broad s, vinyl CH_3, ~20% of the mixture), 1.25 (complex multiplet, 1 cyclopropyl H), 0.5 ppm (complex multiplet, 4 cyclopropyl Hs).

Preparation of 6-Bromo-3-methyl-1,3-hexadiene (4a). A solution of 439 mg (3.91 mmol) of tertiary vinyl carbinol **2a** in 5.0 mL of glacial acetic acid and 1.0 mL of acetic anhydride was added rapidly to a well-stirred mixture of 140 mg (0.74 mmol) of *p*-toluenesulfonic acid monohydrate and 2.46 g (28.8 mmol) of lithium bromide in 20 mL of glacial acetic acid–4.0 mL of acetic anhydride at 15 °C. After 2 min, the reaction was quenched by quickly pouring the solution into a mixture of 150 mL of 4 N aqueous NaOH and 100 g of crushed ice. Extraction[18] of the product with ether, followed by removal of the solvent via distillation at atmospheric pressure through a Vigreux column and subsequent evaporative distillation, afforded 509 mg (75%) of bromide **4a:** bp 65–70 °C (bath temperature, 7.5 mm) [lit.[26] bp 71–72 °C (12 mm)]; >99% pure by VPC analysis,[23] oven temperature 135 °C, retention time 4.1 min; ν_{max} (film) 3100, 1645, 1610, 1270, 1205, 1080, 985, 900 cm^{-1}; δ_{Me_4Si} (CCl_4) 6.91–4.87 (complex pattern, 4 vinyl Hs), 3.32 (triplet, J = 7 Hz, CH_2Br), 2.69 (quartet, J = 7 Hz, CH_2CH=C), 1.83 (broad s, "*Z*" vinyl methyl, ~30% of the mixture), 1.77 ppm (singlet, "*E*" vinyl methyl, ~70% of the mixture).

4-Methyl-3,5-hexadien-1-ol Acetate (4b). A mixture of 484 mg (2.77 mmol) of bromide **4a** and 1.13 g (13.8 mmol) of anhydrous sodium acetate in 10 mL of dry *N,N*-dimethylformamide was stirred at room temperature for 20 h and then at 95 °C (bath temperature) for 3 h. After cooling this mixture to room temperature, it was diluted with 80 mL of water and the product was isolated by extraction[18] with ether. Subsequent evaporative distillation afforded 257 mg (61%) of acetate **4b**:[13] bp 45–60 °C (bath temperature, 0.20 mm); >97% pure by VPC analysis,[23] oven temperature 155 °C, flow 15 mL/min, retention time 6.7 min; ν_{max} (film) 1740 (C=O), 1640 (C=C), 1605 (C=C), 1385, 1365, 1235, 1035, 985, 900 cm^{-1}; δ_{Me_4Si} (CCl_4) 6.98–4.87 (complex pattern, 4 vinyl Hs), 4.05 (triplet, J = 7 Hz, CH_2OAc), 2.46 (quartet, J = 7 Hz, CH_2CH=C), 1.98 [s, OC(=O)CH_3], 1.84 (broad s, "*Z*" vinyl methyl, ~30% of the mixture), 1.77 ppm (singlet, "*E*" vinyl methyl, ~70% of the mixture). Anal. Calcd for $C_9H_{14}O_2$: C, 70.04; H, 9.16. Found: C, 69.77; H, 8.95.

4-Methyl-3,5-hexadien-1-ol *p*-Toluenesulfonate (4d). A solution of 338 mg (3.01 mmol) of alcohol **2a** in 2.0 mL of glacial acetic acid was added rapidly to a well-stirred solution of 2.839 g (14.9 mmol) of *p*-toluenesulfonic acid monohydrate in 28.0 mL of glacial acetic acid and 1.50 mL (15.8 mmol) of acetic anhydride in a flask kept in a constant temperature bath at 15 °C. After 30 s, the reaction was quenched by quickly pouring the solution into a mixture of 175 mL of 4 N aqueous NaOH and 150 g of crushed ice. Extraction[18] of the product with ether, followed by evaporative distillation, afforded 40 mg (12% yield) of colorless oil, bp 40–55 °C (bath temperature, 0.20 mm). VPC analysis[23] (oven temperature 155 °C, flow 15 mL/min) indicated that >98% of the distillate consisted of a mixture of two components: ring-opened alcohol **4c** (retention time 4.1 min) and primary allylic alcohol **3a** (retention time 4.5 min) in a 20:1 ratio, respectively. Chromatography of the residue (384 mg) of 20 mL of silica gel (elution with hexane–8% ether) afforded 137 mg (17% yield)[17] of tosylate **4d** as a mixture of *E*:*Z* stereoisomers: ν_{max} (film) 1648, 1605, 1500, 1365, 1180, 1100, 975, 910, 815, 750, 660 cm^{-1}; δ_{Me_4Si} (CCl_4) 7.52 (AB quartet, 4 aryl H, peaks at 7.82, 7.67, 7.37, 7.23), 6.84–4.85 (complex pattern, 4 vinyl Hs), 3.99 (triplet, J = 7 Hz, CH_2OTs), 2.48 (quartet, J = 7 Hz, CH_2CH=C), 2.44 (s, CH_3), 1.77 (broad s, vinyl CH_3, ~30% of the mixture), 1.69 ppm (broad s, vinyl CH_3, ~70% of the mixture). Anal. Calcd for $C_{14}H_{18}SO_3$: C, 63.11; H, 6.82; S, 12.04. Found: C, 62.84; H, 6.82; S, 12.26.

Acknowledgments. The authors wish to thank Dr. James W. Wilt and Dr. Harvey W. Posvic of Loyola University of Chicago for their helpful suggestions during the course of this project. The assistance of Nancy Casey and Peter Fries in some of the experimental work is also gratefully acknowledged.

Registry No.—**1**, 765-43-5; **2a**, 1072-76-0; (*E*)-**3a**, 61915-38-6; (*Z*)-**3a**, 61915-39-7; (*E*)-**3b**, 61915-40-0; (*Z*)-**3b**, 61915-41-1; (*E*)-**4a**, 61432-68-6; (*Z*)-**4a**, 61432-65-3; (*E*)-**4b**, 61915-42-2; (*Z*)-**4b**, 61915-43-3; (*E*)-**4d**, 61915-44-4; (*Z*)-**4d**, 61915-45-5; sodium acetate, 127-09-3.

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(9) As shown by the data in Table I, entry 1, >96% of the distilled product mixture consisted of cyclopropanoids **3a** and **3b**. In separate experiments, ring-opened acetate **4b** was shown to be stable to the conditions utilized for the reactions listed as entries 1 and 2 in Table I.
(10) Similar product ratios were obtained in an experiment using acetic acid that had been dried by treatment with triacetyl borate in the manner described by A. Pictet and A. Geleznoff, *Ber.*, **36**, 2219 (1903).
(11) J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure", McGraw-Hill, New York, N.Y., 1968, p 259.
(12) The rearranged acetate (**3c**)[8] was characterized by a doublet at δ 4.65 (J = 7 Hz, CH_2OAc), whereas the starting tertiary vinyl carbinol (**2b**) exhibited a sharp singlet at δ 1.57 (CH_3).
(13) M. Julia, S. Julia, and B. Stalla-Bourdillon, *C. R. Acad. Sci.*, **253**, 951 (1961). Acetate **4b** was prepared in this paper using a different procedure.
(14) The residue in the distillation contained ring-opened material, as determined by NMR analysis. Since most of this mixture was tosylate **4d**, sufficient catalyst must be used in the solvolysis or the reaction will cease prior to complete rearrangement of alcohol **2a**, due to depletion of the catalyst.
(15) When lithium perchlorate was used to replace the lithium bromide in this reaction, no product could be isolated, and it was presumed that an elimination reaction had occurred leading to the formation of volatile C-7 hydrocarbons. To substantiate this hypothesis, an additional experiment was run using lithium perchlorate (1 M solution) and *p*-toluenesulfonic acid (0.0125 M solution) in a more nucleophilic solvent system—25:1 (v/v) acetic acid–water. Under these conditions, alcohol **2a** was converted in 68% yield to a horrendous mixture of products, the NMR spectrum of which showed no cyclopropyl absorption. The yield of distilled product (bp 45–60 °C, 0.10 mm) in this reaction was only 10%. VPC analysis indicated a mixture of at least ten components, none in substantial amounts.
(16) Since this reaction was not complete after 30 s at 15 °C, a reaction time of 2 min was used.
(17) The remainder of the material on the column was not identified after it failed to be eluted with hexane–20% ether. Since the NMR spectrum of the distillation residue taken prior to this chromatography closely resembled the spectrum of purified tosylate **4d**, some decomposition may have occurred on the column.
(18) Unless indicated otherwise, the isolation of reaction products was accomplished by pouring the mixture into water or saturated brine and extracting thoroughly with the specified solvent. The combined extracts were washed with saturated aqueous sodium bicarbonate and saturated brine, and dried over anhydrous magnesium sulfate. The solvent was removed from the dried extracts by using a rotary evaporator under reduced pressure. Evaporative distillation refers to bulb-to-bulb (Kugelrohr) short-path distillation. The NMR spectra were recorded with a Varian A-60 NMR spectrometer and infrared spectra were obtained using a Beckman Acculab 1 spectrophotometer. Microanalyses were performed by Micro-Tech Laboratories, Inc., Skokie, Ill.
(19) Available from Aldrich Chemical Co., Inc., Milwaukee, Wis.
(20) Available from Apache Chemicals, Inc., Seward, Ill.
(21) J. Kulesza, J. Gora, and K. Koseska, *Riechst., Aromen, Koerperpflegem.*, 192, 194, 199–200 (1969); *Chem. Abstr.*, **71**, 102020q (1969).
(22) Resolution of the signal peaks between δ 5.31 and 4.83 was not sufficient to allow a simple determination of J_{AB} and the chemical shifts for these two protons.
(23) A 6 ft × 0.125 in. SE-30 column was used for this analysis.
(24) This component was shown by NMR and VPC analysis to be identical with the alcohol (**4c**) obtained by saponification of ester **4b**. Alcohol **4c** was characterized by a triplet at δ 3.52 (J = 7 Hz, CH_2OH). This alcohol has previously been reported by M. Julia, S. Julia, and B. Stalla-Bourdillon (ref 13).
(25) Identified by coinjection of a mixture of the distilled product and an authentic sample of acetate **4b**.
(26) S. Julia, M. Julia, S.-Yu Tchen, and P. Graffin, *Bull. Soc. Chim. Fr.*, 3207 (1964); French Patent 1 310 528 (Nov 30, 1962); *Chem. Abstr.*, **60**, 427e (1963).

Regio- and Stereoselective Reactions of *trans*-5,6-Epoxy-*cis*-cyclodecene[1a]

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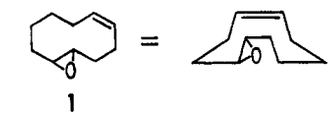
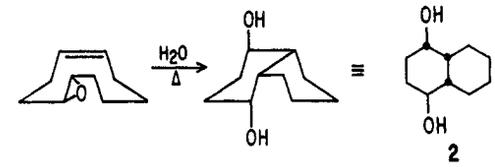
Recent reports on the reactions of acyclic and cyclic unsaturated epoxides with organometallic reagents[1–6] encouraged us to examine the less studied medium-ring congeners, which we felt would reveal novel pathways.[6–9] We found that products from one such epoxide, *trans*-5,6-epoxy-*cis*-cyclodecene[10] (**1**), differ strikingly in structure and selectivity from reaction with one organometallic reagent to another and also from those obtained in aqueous media[11] (see Scheme I). The



1

Scheme I

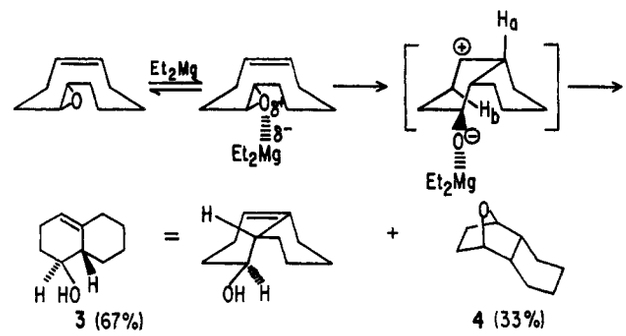


2

high selectivity of two pathways provides facile entry into two challenging ring functionalities of current interest.[9,12]

For example, when **1** is added to diethylmagnesium products **3** and **4** result (Scheme II). Ring opening is facilitated by

Scheme II



3 (67%) **4** (33%)

magnesium ion and occurs at the C_6 position most likely as a result of through-space interaction with the double bond in the transition state.[11,13]

It is somewhat surprising that GC/mass spectrographic analyses failed to reveal addition products for all the Grignard-like reagents tested (ref 14–16 and vide infra). Also interesting is the effectiveness of the weak Lewis acid diethylmagnesium to effect a clean transannular ring closure. For example, reaction of **1** with BF_3·OEt_2 and Grignard reagents yielded synthetically less useful complex mixtures of products. Although **3** was the major product in these cases, additional products resulted from competing rearrangements. In retrospect, this is not unexpected since the magnesium halide in Grignards is known to give competing rearrangement[2–5,8] products, and BF_3·OEt_2 could ring open **4** and lead to carbonium-ion-like rearrangements.

The reaction was shown to be stereoselective for isomer **3** by comparison of physical and spectral constants with those of an authentic sample synthesized by an alternate route.[12] Some $\Delta^{3(4)}$-octalol, detected by NMR, resulted from elimination of a different hydrogen (H_b, Scheme II).[17]

Compound **4**, 1,4-endoxodecalin,[18,19] was identified by establishing its symmetry in hydrogen-decoupled ^{13}C NMR [peaks at δ ^1H 80.1, 40.3, 24.3, and 19.6 ppm in a 1:1:1:2 ratio ($CDCl_3$)]. Also, the ^1H NMR of **4** was similar to that of a model compound, 7-oxabicyclo[2.2.1]heptane [δ 4.4 (CHOCH multiplet)] with multiplets at δ 4.4 (CHOCH) and 1.0–2.1 ppm (m, 14 H).

Whereas **1** underwent stereoselective ring closure with a dialkylmagnesium reagent, it reacted by a different pathway with an organolithium reagent. When freshly prepared phenyllithium was refluxed with **1** in ether, proton abstraction led to **5** in high yields (Scheme III). Bisallylic NMR peaks of