(3) G. C. Levy, J. D. Cargioli, and W. Racela, *J. Am. Chem. Soc.*, **92**, 6238 (1970).
(4) G. A. Olah and A. M. White, *J. Am. Chem. Soc.*, **91**, 5801 (1969).
(5) M. Julia, S. Julia, and R. Guegan, *Bull. Soc. Chim. Fr.*, 1072 (1960).
(6) R. Breslow, "Molecular Rearrangements", P. de Mayo, Ed., Interscience, New York, N.Y., 1967, pp 254–276.
(7) R. G. Pearson and S. H. Langer, *J. Am. Chem. Soc.*, **75**, 1065 (1953).
(8) J. H. Babler and D. O. Olsen, *Tetrahedron Lett.*, 351 (1974). The allylic rearrangements of alcohols **2b** and **2c** were reported in this communication.
(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).

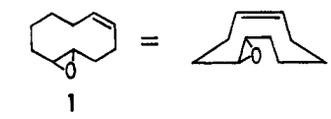
Regio- and Stereoselective Reactions of *trans*-5,6-Epoxy-*cis*-cyclodecene[1a]

Stephen K. Taylor[1b] and Charles B. Rose*

Department of Chemistry, University of Nevada, Reno, Nevada 89557

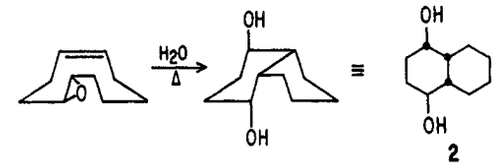
Received October 22, 1976

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

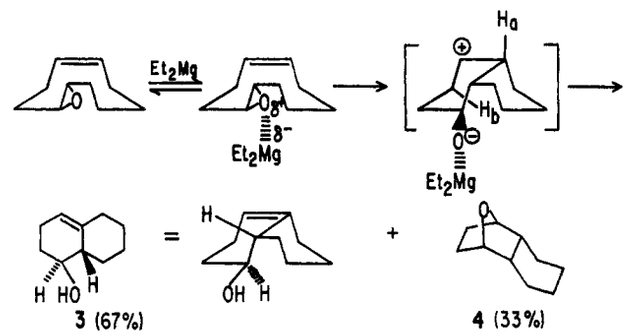


2

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]

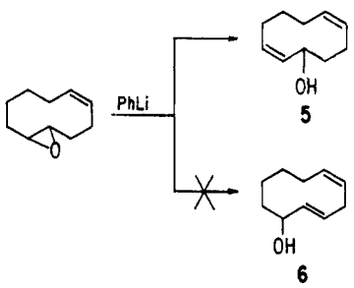
It is somewhat surprising that GC/mass spectrographic analyses failed to reveal addition products for all the Grignard-like reagents tested (ref 14–16 and vide infra). Also interesting is the effectiveness of the weak Lewis acid diethylmagnesium to effect a clean transannular ring closure. For example, 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

Scheme III



6 (Scheme III) were notably absent in all NMR spectra. Equilibration studies[21] and other considerations[22] indicate a strong conformational preference for the formation of **5**. However, ketonic products, whose presence would indicate rearrangement, were notably absent.[20]

These results complement other work with similar compounds[6,11] and help demonstrate the generality of the highly selective reaction pathways possible with unsaturated medium-ring epoxides.

Experimental Section

Reaction of Diethylmagnesium with *trans*-5,6-Epoxy-*cis*-cyclodecene. A solution of 1.52 g (10 mmol) of **1** in 20 mL of ether was added dropwise to 15 mL of an ice-cooled 0.6 M solution of diethylmagnesium.[23] After the solution was refluxed for 15 h, standard workup gave a mixture of **3** and **4** in an 85–90% yield. A sample of **3** was isolated by fractional distillation [bp 91–93 °C (20 mm); $n^{25}D$ 1.4885; NMR (CCl_4) δ 4.3 (multiplet, 2 H) and 1.0–2.1 (multiplet, 14 H); M^+ (calcd) 152.1200 for $C_{10}H_{16}O$, found 152.1188]. Compound **4** was crystallized out of the residue at low temperature from ether/pentane. Its melting point was 40–42 °C; IR and NMR spectra were identical with those of an authentic sample.[12]

Preparation of *cis,cis*-2,7-Cyclodecadienol. Under argon atmosphere, approximately 20 mmol of phenyllithium[24] was freshly prepared in 30 mL of ether. A solution containing 2.28 g (15 mmol) of **1** in 10 mL of ether was added dropwise to the phenyllithium. After 8–12 h reflux, normal workup gave an oil which crystallized after 2 days in the freezer. The crude solid (2.28 g) was recrystallized from 50–70 °C-boiling petroleum ether yielding 1.62 g (72%) of **5** [mp 89.8–90.7 °C; IR (CCl_4) 3200–3650 (OH) and 708 cm^{-1} (cis CH=CH); NMR (CCl_4) δ 5.0–5.6 (m, 4, -CH=CH-), 4.15–4.60 (m, 1, CHO), and 1.1–2.5 (m, 11 remaining H); mass spectrum (75 eV) *m/e* 152 M^+ (10), 55 (94), and 29 (100)].

Anal. Calcd for $C_{10}H_{16}O$; C, 78.89; H, 10.60. Found: C, 78.68; H, 10.72.

Acknowledgments. We wish to thank J. R. Olechowski for a generous sample of *cis,trans*-1,5-cyclodecadiene. P. S. Wharton kindly provided us with NMR and IR spectra of *syn*- and *anti*-$\Delta^{4(10)}$-octalol (**3**).

Registry No.—**1**, 24639-32-5; **3**, 41727-79-1; **4**, 61967-02-0; **5**, 61967-03-1; diethylmagnesium, 557-18-6; phenyllithium, 591-51-5.

References and Notes

(1) (a) Part 3 in the series "The Reactions of Organometallic Reagents with Unsaturated Epoxides". See C. B. Rose and S. K. Taylor, *J. Org. Chem.*, **39**, 578 (1974), for part 2. (b) NDEA Title IV Predoctoral Fellow, 1969–1972; abstracted in part from the doctoral dissertation of S. K. T.
(2) R. J. Anderson, *J. Am. Chem. Soc.*, **92**, 4978 (1970).
(3) R. W. Herr and C. R. Johnson, *J. Am. Chem. Soc.*, **92**, 4979 (1970).
(4) J. Staroscik and B. Rickborn, *J. Am. Chem. Soc.*, **93**, 3046 (1971).
(5) C. R. Johnson, R. W. Herr, and D. M. Wieland, *J. Org. Chem.*, **38**, 4263 (1973).
(6) E. D. Brown, J. K. Sutherland, and T. W. Sam, *J. Chem. Soc., Perkin Trans. 1*, 2332 (1975).
(7) J. Sicher, *Prog. Stereochem.*, **3**, 202 (1962).
(8) A. C. Cope, M. M. Martin, and M. A. McKervey, *Q. Rev., Chem. Soc.*, **20**, 119 (1966).
(9) J. A. Marshall, *Synthesis*, 517 (1972).
(10) J. G. Traynham, G. R. Franzen, G. A. Knesel, and D. J. Northington, Jr., *J. Org. Chem.*, **32**, 3285 (1967).
(11) W. Dittman and F. Stürzenhofecker, *Justus Liebigs Ann. Chem.*, **688**, 57 (1965).
(12) P. S. Wharton and D. W. Johnson, *J. Org. Chem.* **38**, 4117 (1973).
(13) P. Bischof and E. Heilbronner, *Helv. Chim. Acta*, **53**, 1677 (1970).
(14) H. O. House, R. W. Giese, K. Kronberger, J. P. Kaplan, and J. K. Simeone, *J. Am. Chem. Soc.*, **92**, 2800 (1970).
(15) A. J. Birch and M. Smith, *Proc. Chem. Soc., London*, 356 (1962).
(16) G. H. Posner, *Org. React.*, **19**, (1972).
(17) A small vinyl peak at δ 5.5 in the NMR spectrum of **3** was essentially identical with that of the hydrocarbon analogue of $\Delta^{3(4)}$-octalol prepared by dehydration of *cis*-decahydronaphthol.
(18) E. L. Wittbecker, H. K. Hall, Jr., and T. W. Campbell, *J. Am. Chem. Soc.*, **82**, 1218 (1960).
(19) We prepared **2** by the reaction shown in Scheme I and dehydrated it after the method described in ref 18. This method gave the exo isomer of **4** in low yield [NMR (CCl_4) δ 4.0 (m, CHOCH) and 1.0–2.0 (m, 14 H)]. The exo isomer had a narrower CHOCH multiplet than endoxodecalin (the latter compound has exo hydrogens which couple more strongly than the endo hydrogens of the former compound).
(20) See J. K. Crandall and L. C. Lin, *J. Org. Chem.*, **33**, 2375 (1968), and references cited therein.
(21) A. J. Hubert and J. Dale, *J. Chem. Soc. C*, 188 (1968).
(22) B. W. Roberts, J. J. Vollmer, and K. L. Servis, *J. Am. Chem. Soc*, **96**, 4578 (1974).
(23) F. H. Norton and H. B. Hass, *J. Am. Chem. Soc.*, **58**, 2147 (1936).
(24) L. A. Walter, "Organic Syntheses", Collect. Vol. III, Wiley, New York, N.Y., 1955, p 757.

Stereospecific Thallium(III) Nitrate Mediated Conversion of Bicyclo[3.2.1]-2-octanone to *exo*-2-Norbornanecarboxylic Acid Methyl Ester[1a,b]

Anthony J. Irwin[1c] and J. Bryan Jones*

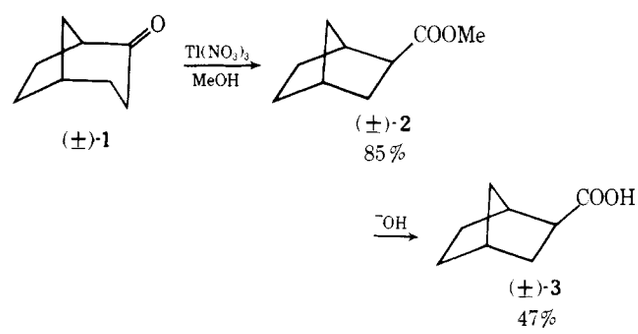
Department of Chemistry, University of Toronto, Toronto, Ontario, Canada M5S 1A1

Received November 9, 1976

During absolute configuration assignments of bridged bicyclic products of some enzymic oxidoreduction reactions,[2] we carried out thallium(III) nitrate in methanol mediated homologation of (1*S*,4*R*)-2-methylenenorbornane to (1*S*,5*S*)-bicyclo[3.2.1]-2-octanone (**1**), a reaction similar to that first reported in the racemic series by Fărcaşiu and coworkers.[3] A methyl ester impurity was also formed in varying amounts during the reaction. This methyl ester, whose proportion we now find can reach as high as 31% under the homologation conditions, has been identified as *exo*-2-norbornanecarboxylic acid methyl ester (**2**).

In view of the examples now available of ring contraction on treatment of six-membered cyclic ring ketones with thallium nitrate,[4–7] it seemed evident that **2** was formed from the initial homologation product **1**. This was confirmed by subjecting **1** itself to the thallium nitrate in methanol conditions. As shown in Scheme I, an 85% yield of **2**, characterized as the acid **3**, was obtained.

Scheme I



As in the steroid series,[6] the ring contraction is highly stereospecific, with none of the endo isomer of **2** being detected.[8] The exclusive formation of the exo ester **2** is consistent with the mechanism proposed by McKillop and Taylor,[5] with attack of the enol intermediate **4** by Tl^{3+} occurring from the exo direction as expected for electrophilic additions of this type.[9] The pathway envisaged is depicted in Scheme II.