washed with small quantities of cold ethanol followed by small quantities of ether. The crude chloropropanones, usually $\sim$10 g, were used directly without further purification. Crude chloropropanone was dissolved in 250 ml of ethanol containing 0.3 mol of piperidine and refluxed for 24 hr. The solvent was evaporated under reduced pressure and the resulting residue was taken up in ether and washed with 5% HCl and with H_2O, dried ($CaSO_4$), and evaporated. The crude residue was placed on a chromatograph column packed with Al_2O_3. The eluent was typically benzene–low boiling petroleum ether mixtures.[12] The *Z* isomers were the first isomers to be eluted. Frequently, to obtain reasonable quantities of the *Z* isomers, benzene solutions of $\sim 10^{-3}$ *M E* isomers were irradiated for 24 hr with a 320-W uv lamp fitted with a 2537-A light source. The product of the irradiation was chromatographed as described above. The physical properties of the α-phenylchalcones prepared in this way are listed in Table V.

Table V contains melting points obtained with a Thomas-Hoover Uni-Melt and they are corrected. Also, Table V contains uv data obtained for the α-phenylchalcones in $\sim 10^{-5}$ *M* absolute ethanol solutions on a Beckman DK-2 spectrometer. Analyses were obtained by Atlantic Microlab, Atlanta, Ga.

Registry No.—**1**, 34236-57-2; **2**, 34236-58-3; **3**, 34236-59-4; **4**, 34236-60-7; **5**, 7512-67-6; **6**, 34236-62-9; **7**, 34236-63-0; **8**, 34236-64-1; **9**, 34236-65-2; **10**, 34236-66-3; **11**, 34236-67-4; **12**, 34236-68-5; **13**, 7474-65-9; **14**, 34236-70-9; **15**, 34236-71-0; **16**, 34236-72-1.

Acknowledgments.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We wish to thank Professor R. E. Lutz for samples of **8** and **16**.

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[12] *Cf.* L. E. Friedrich and R. A. Cormier, *J. Org. Chem.*, **35**, 450 (1970).

Notes

The Rearrangement of 11,11-Dibromotricyclo[4.4.1.0^{1,6}]undecane

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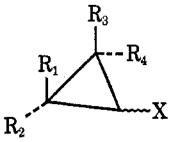
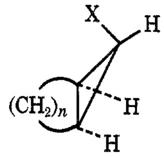
Received November 4, 1971

The solvolysis of various monocyclic and bicyclic cyclopropyl compounds has received widespread attention by numerous investigators during the past several years.[1] The impetus for this interest arises, for the most part, from the elegant and far-reaching theories of Woodward, Hoffmann, and DePuy concerning the electrocyclic reactions of cyclopropyl systems.[2] Product as well as kinetic studies have unequivocally demonstrated that in secondary, monocyclic systems (*e.g.*, **1**) electrocyclic opening during solvolysis proceeds in a concerted disrotatory fashion with the alkyl substituents trans to the leaving group rotating outward and those cis to the leaving group rotating inward.[1,3] These experimental findings are in complete agreement with theory.[2] In the bicyclic endo system **2**, again, experiment verifies theory. That is, solvolysis proceeds in a disrotatory fashion affording a cis-allyl cation, which is subsequently quenched by solvent. In the corresponding exo series **3**, experiment seems to support the intermediary of a "partially opened" cyclopropyl cation **4** which leads to cyclopropyl, cis-allyl, or trans-allyl products (or products derived from trans-allyl derivatives) when $n \leq 5$. The relative yields of these products depend on the magnitude of n and the reaction conditions. For those cases in which $n > 5$ only monocyclic allyl products are obtained, since the ring structure is now large enough to accommodate a transition state approaching that of the monocyclic series.[1,4–7]

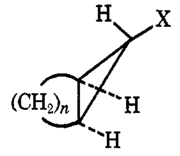


1

X = halogen, -OTs, -OTf

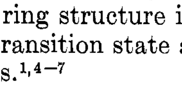


2



3

X = halogen, -OTs, -OTf



4

Substitution of a group which can stabilize a positive charge at the site of the leaving group (*e.g.*, c-Pr or Ph) results primarily in formation of cyclopropyl prod-

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[1] (a) P. v. R. Schleyer, W. F. Sliwinski, G. W. Van Dine, U. Schöllkopf, and J. Paust, *J. Amer. Chem. Soc.*, **94**, 125 (1972), and references contained therein; (b) T. M. Su, Ph.D. Thesis, Princeton University, 1970; (c) W. F. Sliwinski, T. M. Su, and P. v. R. Schleyer, *J. Amer. Chem. Soc.*, **94**, 133 (1972).

[2] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, Weinheim/Bergstr., Germany, 1970.

[3] P. v. R. Schleyer, T. M. Su, M. Saunders, and J. C. Rosenfeld, *J. Amer. Chem. Soc.*, **91**, 5174 (1969).

[4] G. H. Whitham and M. Wright, *Chem. Commun.*, 294 (1967).

[5] U. Schöllkopf, K. Fellenberger, M. Patsch, P. v. R. Schleyer, T. M. Su, and G. W. Van Dine, *Tetrahedron Lett.*, 3639 (1967).

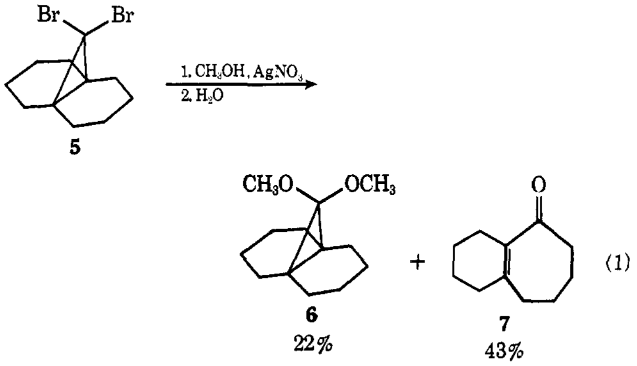
[6] D. T. Clark and G. Smale, *J. Chem. Soc.*, 1050 (1969).

[7] D. Schober, Ph.D. Thesis, University of Chicago, 1969.

ucts.[6-10] Evidence has been presented which is consistent with the formation of a cyclopropyl cation intermediate in these cases.[6]

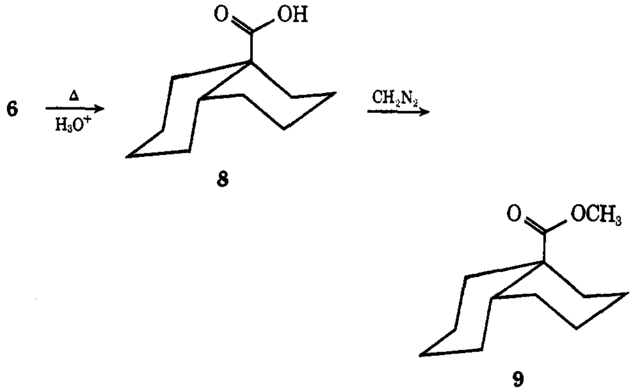
In this paper we report the products obtained in the silver ion assisted methanolysis of the title compound **5**. Compound **5** is constructed such that disrotatory ring opening to a fully opened allyl cation is prohibitive. In addition the electron-withdrawing effect of an α-bromo substituent is not conducive to the stabilization of a cyclopropyl cation. It was conceived that these effects acting in concert would force the system to undergo a Wagner–Meerwein rearrangement, a reaction pathway which heretofore has not been observed in the solvolysis of cyclopropyl derivatives with the leaving group bound directly to the ring.[11]

Compound **5** was synthesized by previously published methods.[13] Its melting point and infrared spectrum were identical with those of an authentic sample.[14] Treatment of **5** with methanolic silver nitrate, followed by an aqueous work-up, resulted in the formation of two major volatile products, **6** and **7**, and several minor components whose structures have not been elucidated (eq 1).



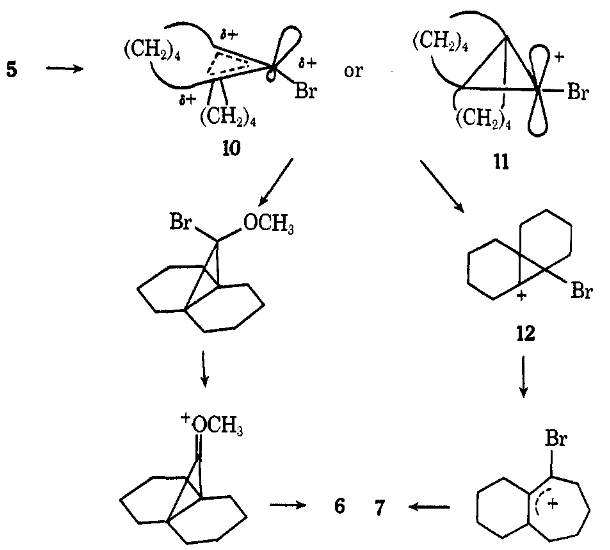
The structure of compound **6** was assigned initially on the basis of its nmr and infrared spectrum in addition to a correct elemental analysis. Unambiguous chemical proof of structure was obtained as outlined in Scheme I. An infrared spectrum of **9** was identical with that of an authentic sample.[15] The structure of compound **7** was assigned on the basis of spectral evidence, a correct elemental analysis, and a molecular ion at *m/e* 164 in the mass spectrum. The nmr spectrum of **7** exhibits absorption at 1.3–1.8 (multiplet, eight protons) and 1.8–2.6 ppm (multiplet, eight protons). No vinyl absorption was observed. In addition the infrared spectrum of **7** exhibits absorption at 1660 and 1630 cm^{-1} (characteristic of C=C—C=O).[16]

SCHEME I



Whether the products obtained in this study arise from a discrete cyclopropyl cation **11** or a partially opened cation **10** we cannot say at this point; however, current theory would seem to favor the latter.[1] The formation of **7** can be rationalized as arising through a Wagner–Meerwein rearrangement of the initially formed cationic species to a more stable cation which (lacking the steric constraints placed on **10** or **11**) undergoes disrotatory ring opening to the cis allyl ion **12**, the precursor to **7** (see Scheme II). Our initial conjecture concerning the feasibility of a Wagner–Meerwein rearrangement thus seems to be correct for this particular system.

SCHEME II[18]



Experimental Section[19]

11,11-Dibromotricyclo[4.4.1.0^{1,6}]undecane (5).—Compound **5** was prepared according to previously published procedures,[13] mp 43–44° (pentane).[14]

Silver Ion Assisted Methanolysis of 5.—Compound **5** (0.49 g, 1.65 mmol) was added to a solution of silver nitrate (0.6 g, 3.30 mmol) in 50 ml of methanol. The resulting solution was then

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[8] D. B. Ledlie and E. A. Nelson, *Tetrahedron Lett.*, 1175 (1969).

[9] D. B. Ledlie and W. H. Hearne, *ibid.*, 4837 (1969).

[10] J. A. Landgrebe and L. W. Becker, *J. Amer. Chem. Soc.*, **90**, 395 (1968).

[11] Applequist has reported a possible mechanism for the deamination of spiropentylamine which involves a Wagner–Meerwein rearrangement of the type we have reported. However, in light of the current theory of electrocyclic reactions this seems unlikely.[12]

[12] D. E. Applequist, and G. F. Fanta, *J. Amer. Chem. Soc.*, **82**, 6393 (1960).

[13] R. Vaidyanathaswamy and D. Devaprabhakana, *Chem. Ind. (London)*, **16**, 515 (1968).

[14] W. R. Moore, private communication.

[15] We are indebted to Professor F. D. Greene for supplying us with an infrared spectrum of compound **9**.

[16] Numerous attempts were made to dehydrogenate *trans*-bicyclo[5.4.0]undecan-2-one with both selenium dioxide and seleneous acid (in various solvents) using the method of Ginsburg in an attempt to synthesize an authentic sample of **7**.[17] However, all our efforts met with failure. We feel, however, that the structure assigned on the basis of the above evidence and mechanistic considerations is unambiguous.

[17] D. Ginsburg and W. J. Rosenfelder, *Tetrahedron*, **1**, 3 (1957).

[18] Both **12** and **13** are depicted as localized cyclopropyl cations since both are tertiary and stabilized in relation to **10**.

[19] Infrared spectra were determined with a Perkin-Elmer Model 457 recording spectrophotometer. The nmr spectra were measured at 60 Hz with an Hitachi Perkin-Elmer R20 spectrometer using tetramethylsilane as an internal reference. All spectra were measured in carbon tetrachloride unless otherwise stated. Magnesium sulfate was employed as the drying agent. All reactions involving air- or moisture-sensitive compounds were carried out under a nitrogen atmosphere.

stirred for 12 hr at room temperature. The reaction mixture was filtered (removal of AgBr), and water was added to the filtrate. The resulting mixture was extracted with 3 × 25 ml of pentane; the extracts were dried and concentrated to yield 0.32 g of a light yellow oil which was subjected to gas chromatographic analysis (vpc). Two major components (**6** and **7**) were shown to be present which were collected.

Compound **7** exhibited nmr and infrared absorption consistent with the assigned structure as well as a molecular ion in the mass spectrum at *m/e* 164. (see text).

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.82. Found: C, 80.23; H, 9.86.

An nmr spectrum of **6** exhibits absorption at 3.18 (singlet, six protons) and 1.00–2.01 ppm (multiplet, 16 protons)

Anal. Calcd for $C_{13}H_{22}O_2$: C, 74.23; H, 10.55. Found: C, 74.08; H, 10.56. The absolute yields of **6** and **7** were determined by vpc to be 22 and 43%, respectively.[20]

Acid Hydrolysis of 11,11-Dimethoxybicyclo[4.4.1.0^{1,6}]undecane (6).—Compound **6** (50 mg, 2.58 mmol) was dissolved in 50 ml of 75% aqueous dioxane with a trace of *p*-toluenesulfonic acid. The resulting solution was refluxed for 3 days. A gas chromatogram of the reaction mixture containing an internal standard, showed that 75% of the starting material had been consumed, and that none of **7** had been formed. The reaction mixture was basified and extracted with ether. The ether extracts were dried and concentrated to afford a light brown solid whose infrared spectrum was characteristic of a carboxylic acid (**8**).

Esterification of Crude Acid 8.—The crude solid obtained above was dissolved in 50 ml of ether and cooled to 0°. Diazomethane in ether was added dropwise with stirring to the cooled solution until a yellow color persisted. Cold, dilute acetic acid was then added to decompose the excess diazomethane and the reaction was worked up in the usual manner. A yellow oil was obtained which exhibited a single peak on gas chromatographic analysis. The material was collected and its infrared spectrum measured. It was identical with an authentic sample of methyl *cis*-9-decalyl carboxylate.[15]

Registry No.—**5**, 20564-71-0; **6**, 34201-85-9; **7**, 27332-61-2.

Acknowledgment.—Acknowledgment is made to the Research Corporation for support of this research.

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[20] A 3 ft × 0.25 in. 10% Carbowax 20M column was employed. Biphenyl was used as the internal standard.

A Novel Cyclization Mediated by Organocopper Reagents

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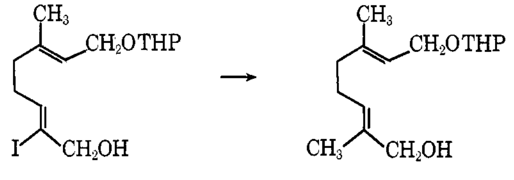
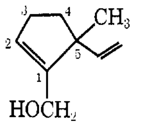
During the course of a synthesis of sirenin,[1] it was observed that the exposure of the iodo ether **1** to dimethylcopperlithium produced in addition to the expected[2] methylation product **2** (30% yield) three other compounds. These by-products, which account for 60% of the mass balance and which appear as a single spot by thin layer chromatography (R_f slightly higher than **2**), have been separated by gas chromatography and identified by spectral methods as **3**, **4**, and **5** (ratio 50:45:5, respectively). The formation of the latter two products is interesting since tetrahydropyranyl ethers, which are normally not regarded as good anionic leaving groups and which are commonly used for protection in organometallic reactions, participate in cross coupling[3] with organocopper reagents. The allylic nature of the tetrahydropyranyl ether **1** must be at least partially responsible for this reactivity.[4] It is also possible that the free hydroxyl group in **1** may play an important role since its conversion to alkoxide might cause tight complex formation with the organometallic reagent or aggregate and so induce a reaction which would normally occur only slowly or not at all. Of even greater significance, however, is the cyclization to the cyclopentene derivative **3**, which is a novel and highly provocative process, and certainly deserving of further investigation. In a formal sense this cyclization is an intramolecular vinyl–allyl coupling, and as such it may prove to have significant generality.[5,6]



1 **2**



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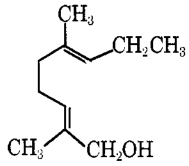

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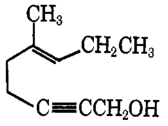

5

Experimental Section

Reaction of Dimethylcopperlithium with 2-Iodo-6-methyl-(2′-tetrahydropyranyloxy)-*trans,trans*-2,6-octadien-1-ol (1).—A flask containing 1.95 g (10.32 mmol) of cuprous iodide was flushed thoroughly with nitrogen and placed in an ice bath, and 75 ml of ether was added. Methyllithium (20.55 mmol, 12.7 ml of a 1.62 *M* ether solution) was added over a 5-min period, and stirring was continued for 10 min after addition was complete. 2-Iodo-6-methyl-8-(2′-tetrahydropyranyloxy)-*trans,trans*-octadien-1-ol (**1**) (300 mg, 0.825 mmol) in 3 ml of ether was added, and the reaction vessel was placed in a 5° cold room and stirred for 30 hr, during which time the reaction mixture changed in color from pale yellow to dark green. The solution was poured over ice–water (considerable bubbling) and filtered through a pad of Celite 545 to remove insoluble copper salts, and the organic layer, combined with four extracts of the aqueous layer, was dried over sodium carbonate (and briefly over $MgSO_4$), filtered, and concentrated to *ca.* 160 mg of an oil. This crude product showed spots of R_f 0.72 and 0.36 on analytical tlc (1:1 hexane–ether, two developments), and these two components were separated by preparative tlc (pH 8, 1:1 hexane–ether). The more polar material thus isolated (62 mg, 30%) was identified as the expected methylation product **2**, since spectral and analytical data for it were identical with those of authentic **2** prepared by an alternative procedure.[1]

Gas chromatographic (gc) analysis (Carbowax 20M column

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[1] See E. J. Corey, K. Achiwa, and J. A. Katzenellenbogen, *J. Amer. Chem. Soc.*, **91**, 4318 (1969).

[2] E. J. Corey and G. H. Posner, *ibid.*, **89**, 3911 (1967).

[3] See, for example, (a) E. J. Corey, J. A. Katzenellenbogen, and G. H. Posner, *ibid.*, **89**, 4245 (1967); (b) E. J. Corey, J. A. Katzenellenbogen, N. W. Gilman, S. A. Roman, and B. W. Erickson, *ibid.*, **90**, 5618 (1968).

[4] Epoxides and allylic acetates have also been found to react readily with organocopper reagents. See (a) R. J. Anderson, C. A. Henrick, and J. B. Siddall, *ibid.*, **92**, 735 (1970); (b) P. Roma and P. Crabbe, *ibid.*, **91**, 3289 (1969); (c) R. J. Anderson, *ibid.*, **92**, 4978 (1970); R. W. Herr, D. M. Wieland, and C. R. Johnson, *ibid.*, **92**, 3813 (1970).

[5] For other recently discovered cyclization reactions using organocopper reagents, see (a) E. J. Corey and I. Kuwajima, *ibid.*, **92**, 395 (1970), and (b) E. J. Corey, M. Narisada, T. Hiraoka, and R. A. Ellison, *ibid.*, **92**, 396 (1970).

[6] This study was assisted financially by the National Institutes of Health and the National Science Foundation.