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.

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

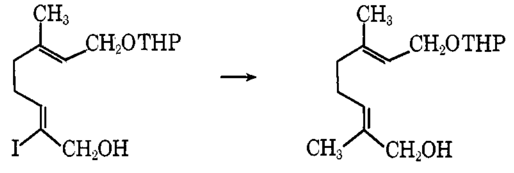
A Novel Cyclization Mediated by Organocopper Reagents

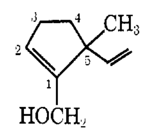
JOHN A. KATZENELLENBOGEN AND E. J. COREY*

Department of Chemistry, Harvard University, Cambridge, Massachusetts 02138

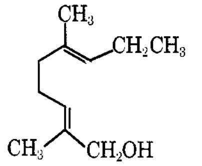
Received September 17, 1971

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]

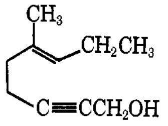




3



4



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

---

[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.

at 125°) of the less polar fraction obtained in the preceding reaction showed three components with retention times of 2.3 min (45%, component A), 5.7 min (50%, component B), and 9.2 min (5%, component C). These materials were separated by preparative gc (Carbowax 20M + KOH column at 180°) and were assigned structures **3**, **4**, and **5** on the basis of spectral data (obtained for gas chromatographically homogeneous samples): component A, 1-hydroxymethyl-5-methyl-5-vinylcyclopentene (**3**); component B, 2,6-dimethyl-*trans*,*trans*-2,6-nonadien-1-ol (**4**); and component C, 6-methyl-*trans*-6-nonen-2-yn-1-ol (**5**).

The alcohol **3** showed the following nmr spectrum (CCl_4): 1.15 (singlet, 3 H, CH_3–), 1.55–1.95 (multiplet, 2 H, –CH_2–, C-4), 2.1–2.45 (multiplet, 2 H, –CH_2–, C-3), 3.78 (singlet, 1 H, –OH), 3.94 (broad singlet, 2 H, –CH_2O–), 4.90 (doublet, J = 18 Hz, 1 H, –CH=C(H)**H**, cis to cyclopentene ring), 4.90 (doublet, J = 10 Hz, 1 H, –CH=C(H)**H**, *trans* to cyclopentene ring), 5.60 (1 H, =CH–, C-2), and 5.81 (doublet of doublets, J = 10, 18 Hz, 1 H, –C**H**=CH_2). The ir spectrum (CCl_4) exhibited bands at 3.05 (s, O–H stretch), 3.40 and 3.50 (s, C–H stretch), 6.10 (m, C=C stretch), 6.90, 7.10, and 7.30 (m, C–H bend), 9.15 (m), 9.70 (s, C–O stretch), 9.95 and 10.9 (s, C–H out of plane deformation, –CH=CH_2), and 12.65 (m). The mass spectrum (20 eV) showed a molecular ion at *m/e* 138, with prominent peaks resulting from cleavage of the fragments CH_3 (123), H_2O (120), CH_2OH (107), and H_2O + CH_3 (105), as well as other peaks at *m/e* 96, 94, 92, and 79.

An exact mass determination (AEI MS-9 mass spectrometer) showed the parent peak at *m/e* 138.1040 (calcd for $C_9H_{14}O$: 138.1044).

The nmr spectrum (CCl_4) of **4** exhibited signals at 0.94 (triplet, J = 7.5 Hz, 3 H, CH_3CH_2–), 1.60 (singlet, 6 H, CH_3C=), 1.75–2.3 (multiplet, 6 H, –CH_2–, C-4, 5, 8), 2.49 (singlet, 1 H, –OH), 3.85 (singlet, 2 H, –CH_2O–), 5.09 (triplet, J = 6 Hz, 1 H, =CH–, C-7), and 5.31 (triplet, J = 6 Hz, 1 H, =CH–, C-3). The ir spectrum (liquid film) revealed bands at 3.00 (s, O–H stretch), 3.40 and 3.50 (s, C–H stretch), 5.98 (w, C=C stretch), 6.90 and 7.20 (m, C–H bend), 7.65 (w), 8.20 (w), 8.65 (w), 9.30 (m), 9.85 (s, C–O stretch), and 11.60 (m).

The nmr spectrum (CCl_4) of **5** exhibited resonances at 0.94 (triplet, J = 7.5 Hz, 3 H, CH_3CH_2–), 1.60 (singlet, 3 H, CH_3–C=), 1.8–2.4 (multiplet, 7 H, –CH_2–, C-4, 5, 8, and –OH), 4.11 (singlet, 2 H, –CH_2O–), and 5.14 (triplet, J = 6 Hz, 1 H, =CH–). The ir spectrum (liquid film) displayed absorbence maxima at 3.0 (s, O–H stretch), 3.40 and 3.50 (s, C–H stretch), 4.37 and 4.40 (w, C≡C stretch), 6.00 (w, C=C stretch), 6.90 and 7.25 (m, C–H bend), 8.15 (m), 8.80 (s), and 9.80 (s, C–O stretch).

Registry No.—**1**, 33835-56-2; **3**, 33835-15-3; **4**, 33835-57-3; **5**, 33835-58-4; dimethylcopperlithium, 15681-48-8.

Mechanism of the Base-Catalyzed Condensation of Naphthols with 2,3-Dichloro-1,4-naphthoquinone

F. D. Saeva

Xerox Corporation, Rochester Corporate Research Center, Webster, New York 14580

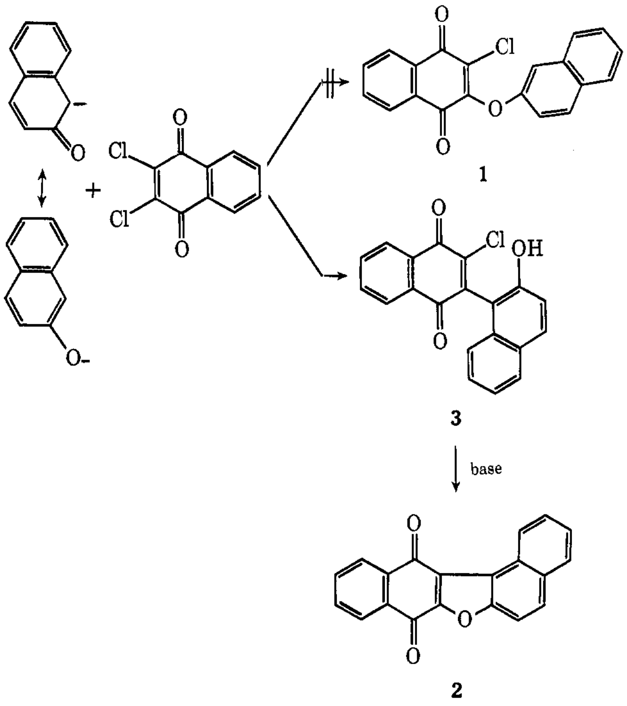
Received July 29, 1971

Dinaphthofurandiones, more commonly called benzobrazanquinones, are a series of heterocyclic quinones derived from the base-catalyzed condensation of 1- or 2-naphthol with 2,3-dichloro-1,4-naphthoquinone (DCNQ). The synthesis of dinaphthofurandiones has been reported[1,2] to proceed *via* initial O alkylation of the naphthol anion to yield compound **1**, in the case of 2-naphthol, which then cyclizes, under the reaction conditions, to provide dinaphtho[2,1:2′,3′]furan-8,13-dione (**2**).

Since the reported cyclization of **1** to **2** did not appear reasonable and consistent with the poorly nucleophilic character of the one position of the naphthyl ether, the base-catalyzed condensation of 2-naphthol with DCNQ was investigated.

A red crystalline compound was isolated from the reaction of 2-naphthol with DCNQ in 2-propanol, using 1 mol of sodium acetate, and was proven to be the intermediate by the cyclization to **2** in refluxing pyridine. The intermediate displays an OH stretching frequency at 3575 cm^{-1} in dioxane and treatment of an aqueous acetone solution with alkali produces a blue-colored anion [λ_{max} = 670 mμ ($\epsilon \sim 4000$)], which converts to compound **2** after several minutes at room temperature. Compound **2** decomposes under these basic conditions in a secondary process, providing 2-naphthol and several other compounds which were not identified.

Thus, the intermediate is indicated to be the product of C alkylation (**3**) where a route for ring closure and dinaphthofurandione formation is clearly provided.



Dinaphthofurandione formation then involves initial alkylation on the 2-naphthol anion one position rather than an oxygen, consistent with the greater nucleophilicity of C *vs.* O bases in polar solvents.[3]

This mechanism is also consistent with the inability to form benzo[*b*]naphtho[2,3-*d*]furan-6,11-dione from the condensation of phenol with DCNQ[4] and also the ease of the preparation of certain substituted benzonaphthofurandiones in which meta-substituted phenols are condensed with DCNQ.[2] In these cases strongly electron-donating substituents such as methoxy or dimethylamino, which favor C alkylation, must be employed. If condensation occurs initially by heteroatom attack, as in the case of the addition of aniline to

---

[1] R. V. Acharya, B. D. Tilak, and M. R. Venkiteswaran, *J. Sci. Ind. Res.*, **16B**, 400 (1957).

[2] M. F. Sartori, *Chem. Rev.*, **63**, 279 (1963).

[3] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, p 259.

[4] R. Gruber, private communication.