ference, 11.5 kcal mol^{-1}, approximates the molecular electronic destabilization associated with the homoantiaromaticity of bicyclopentene.

The hot-molecule effects observed in the thermal isomerizations of bicyclopentenes[23-25] have been analyzed in terms of RRKM theory and the Benson–O'Neal estimate of $\Delta H_f°$ for bicyclopentene.[19] The higher energy of the molecule connected with homoantiaromaticity implies that a reanalysis would need to employ a more efficient collisional deactivation parameter and a more negative $\Delta H°$: the transition-state region for the bicyclopentene-to-cyclopentadiene thermal isomerization[26] is some 73.6 kcal mol^{-1} above ground-state cyclopentadiene.

Further study of bicyclopentene and consideration of the concepts of antiaromaticity[27] and homoantiaromaticity seem warranted.

Acknowledgment. We are grateful to Dr. Göran Ahlgren (Royal Institute of Technology, Stockholm) and Dr. Melvin Goldstein (Cornell University, Ithaca) for helpful correspondence and to the National Science Foundation for financial support.

Registry No. bicyclo[2.1.0]pent-2-ene, 5164-35-2.

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2,5-Dimethyl-3-furoic Acid, a Companion to Feist's Acid in the Reaction of 3-Bromo-5-(carboethoxy)-4,6-dimethyl-2-pyrone with Alkali

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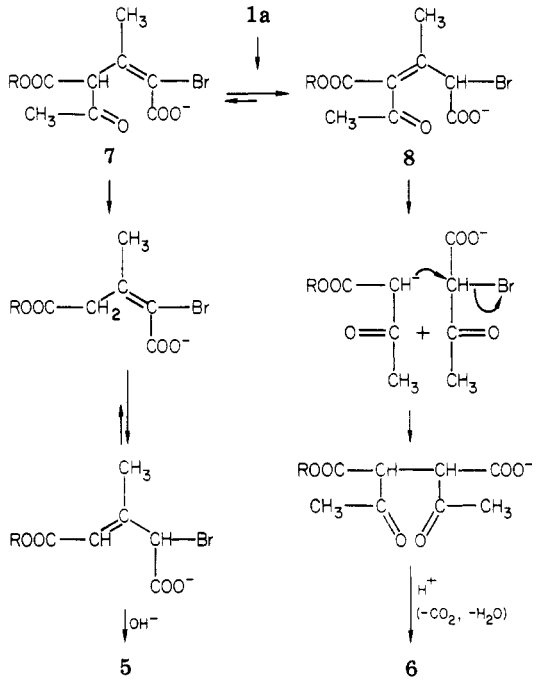
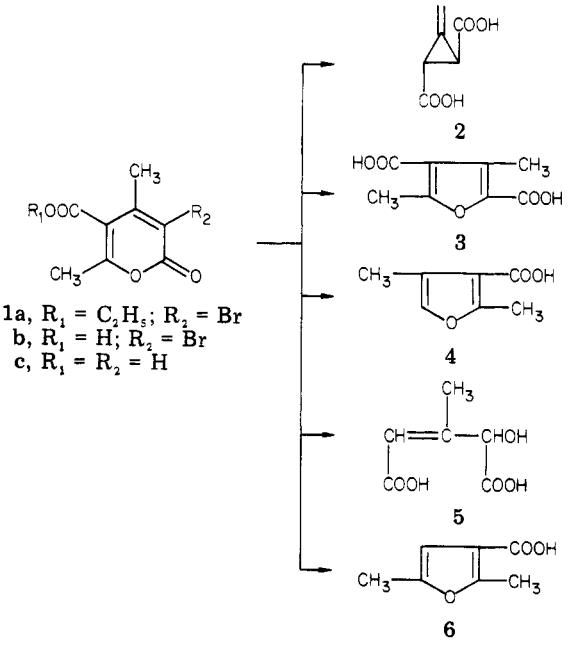
In 1893 Feist described the isolation of a dicarboxylic acid containing a three-membered ring from the treatment of ethyl bromoisodehydroacetate (3-bromo-5-(carboethoxy)-4,6-dimethyl-2-pyrone, **1a**) with alkali[1] but the structure of this acid (Feist's acid) was not securely established until 1952 when Ettlinger proved it to be 3-methylenecyclopropane-*trans*-1,2-dicarboxylic acid (**2**).[2,3]

Feist also reported that the bromo acid **1b** yielded 2,4-dimethylfuran-3,5-dicarboxylic acid (**3**) upon treatment with alkali and that the bromination in water of isodehydroacetic acid (**1c**) itself yielded 2,4-dimethyl-3-furoic acid (**4**).[1] More recently, a reinvestigation of the reaction of 3-bromo-2-pyrones with bases confirmed the earlier results and further disclosed that 3-hydroxy-2-methylpropene-1,3-dicarboxylic acid (**5**) was also formed in the reaction of **1a** in 20% aqueous KOH at 20 °C.[4] No explanation was provided for this transformation.

We now report that yet another furoic acid is obtained when **1a** is treated with boiling 16% aqueous KOH and the reaction products are esterified and distilled. The lower boiling fraction yields one major component, which gives crystalline 2,5-dimethyl-3-furoic acid (**6**) after saponification. This product was identified by direct comparison with an authentic sample.[5]

Scheme I





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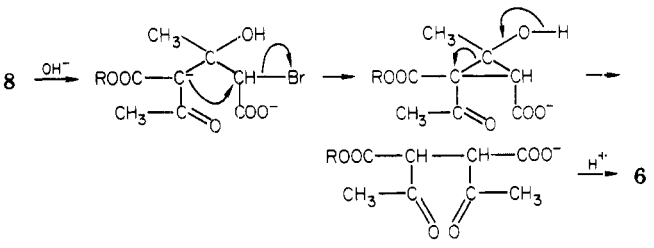
Scheme II



At first, the above synthesis of **6** from **1a** was quite puzzling, since the two methyl groups in the product are separated by four carbon atoms, while the methyl groups in the starting material from which they most certainly originate are separated by only three carbon atoms. However, as shown in Scheme I, there is a mechanism which explains the synthesis of both **5** and **6** from **1a**. It is based on the initial base-catalyzed opening of **1a** into the tautomeric glutaconic acid derivatives **7** and **8**. Further attack by one hydroxide ion onto the ketone carbonyl of **7** will induce the loss of the acetyl group, and displacement of the bromine and saponification will complete the synthesis of **5**.

Base-catalyzed retroaldol cleavage of **8** will lead to the enolate ion of ethyl acetoacetate and to potassium 2-bromoacetoacetate. The alkylation of the latter by the former, followed by an acid-catalyzed cyclization and decarboxylation explains the formation of **6**. It has not been determined whether the decarboxylation precedes the alkylation or even whether the whole process occurs intramolecularly after the addition of the hydroxide ion onto **8**, as shown in Scheme II.

The synthesis of the furoic acid **6** from **1a** appears to be quite sensitive to the base concentration, and a survey where it was varied from 0.01 M to 40% showed that our initial reaction conditions were fortuitously optimal.

Experimental Section

Molten ethyl bromoisodehydroacetate (94 g) was added at once to a boiling solution of 155 g of KOH pellets in 770 mL of water. After the vigorous reaction had subsided, the solution was cooled, acidified, and extracted with EtOAc. The extract was dried and concentrated, and the residue was esterified with ethanol in the presence of H_2SO_4. After workup, the organic products were distilled at 0.03 torr, yielding a fraction (9.25 g) boiling at 30–90 °C and 17 g of Feist's ester, bp 90–100 °C. The forerun was redistilled at 70 °C (1.9 torr). Its acid-catalyzed hydrolysis led to decomposition, but its saponification yielded crystalline 2,5-dimethyl-3-furoic acid, mp 135.9–136.4 °C (this increased to 138.9–139.1 °C after several recrystallizations from aqueous ethanol). The yield from **1a** was about 3%.

For comparison, the sodium salt from 30.4 g of ethyl acetoacetate was treated with 21.3 g of bromoacetone.[5] After distillation, the fraction boiling at 110 °C (2 torr) was treated with cold concentrated H_2SO_4. After workup and saponification of the product, 5.05 g of **6**, mp 136.8–138 °C, was obtained, which was identical with the above product (mp, mmp, and IR).

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Registry No. **1a**, 18152-79-9; **2**, 499-02-5; **4**, 15058-72-7; **6**, 636-44-2; ethyl acetoacetate, 141-97-9; bromoacetone, 598-31-2.

Marine Natural Products: Dihydroxydeodactol Monoacetate, a Halogenated Sesquiterpene Ether from the Sea Hare *Aplysia dactylomela*[1]

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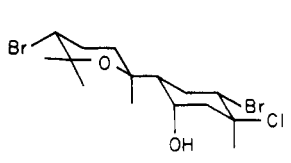
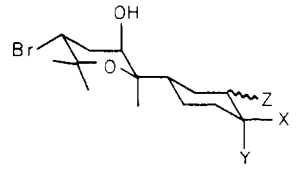
In an earlier report[2] we described the structure elucidation by X-ray analysis of the mildly cytotoxic sesquiterpenoid deodactol (**1**) isolated from the opisthobranch mollusc *Aplysia dactylomela*. The ether **1** is closely related to caespitol[3a] (**2**) and isocaespitol[3b] (**3**) which were isolated from the alga *Laurencia caespitosa*. A number of other algal metabolites have also been isolated[4] from *A. dactylomela* which, like other sea hares, thrives on algae and concentrates many algal metabolites, some of which are presumably used for chemical defense.[5] In this note we report that further investigation of the extracts of *A. dactylomela* from Bimini, Bahamas, has led to the discovery of a more oxygenated form of **1**, namely dihydroxydeodactol monoacetate, **4**.



1



2, X = Cl; Y = CH_3; Z = Br (e)
3, X = CH_3; Y = Br; Z = Cl (a)

The new sesquiterpenoid was isolated from alcohol extracts of sea hare digestive glands by solvent partitioning followed by Sephadex LH-20 and silica gel chromatography as described for 14-bromoobtus-1-ene-3,11-diol.[4a] Dihydroxydeodactol monoacetate (**4**), mp 168–169 °C, $[\alpha]_D$ +40.5° ($CHCl_3$), was assigned the molecular formula $C_{17}H_{27}O_5Br_2Cl$ on the basis of mass spectral data: low resolution, *m/e* 504, 506, 508, 510 (M^+); high resolution, see Experimental Section. The infrared spectrum contained hydroxyl absorption at 3440 cm^{-1} and a single, sharp carbonyl absorption at 1730 cm^{-1} attributable to an acetate group. The ^1H NMR spectrum confirmed the presence of a single acetate group (δ 2.14, 3 H, s) and also contraindicated any carbon–carbon unsaturation, since there were no olefinic proton signals. Hence, it was concluded that **4** was probably bicyclic.

The ^1H NMR spectrum of **4** resembled that of deodactol (**1**) and immediately suggested a close similarity between the two compounds. Four quaternary methyl signals were

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