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Photochemical Lumiketone-Type Rearrangement of 3-Methoxyphenol Promoted by AlBr$_3$

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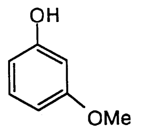
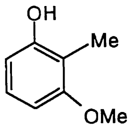
Synopsis. Irradiation of 3-methoxyphenol in the presence of 2 equiv of AlBr$_3$ in CH$_2$Cl$_2$ gave 4-methoxybicyclo[3.1.0]hex-3-en-2-one in a 38% yield. 3-Methoxy-2-methylphenol also yielded the lumiketone rearrangement product. On the other hand, 3-methoxy-4-methyl-, 3-methoxy-5-methyl-, and 5-methoxy-2-methylphenol underwent transposition of the methyl group to give equilibrium mixtures of the three methoxycresols.

Protonated alkyl-substituted phenols have been shown to undergo lumiketone-type photorearrangement which was effected by a Brønsted acid (FSO$_3$H, CF$_3$SO$_3$H) or a Lewis acid (AlBr$_3$, aluminosilicates) giving bicyclo[3.1.0]hex-3-en-2-ones.[1] This rearrangement is analogous to the well-known isomerizations of 2,5-cyclohexadienones[2] and provides a useful method for the preparation of bicyclo[3.1.0]hex-3-en-2-ones. Although a variety of methyl-substituted phenols undergo this transformation successfully, there seems to be no reports on those with functional groups other than alkyl moieties on the phenol ring. In the present paper, we describe the isomerization of 3-methoxyphenols **1a** and **1b** to the corresponding 4-methoxybicyclo[3.1.0]hex-3-en-2-ones **2a** and **2b**.[3] Since the products **2a** and **2b** possess a β-methoxy-α,β-enone functionality, they could serve as versatile synthetic intermediates for further manipulation.


1a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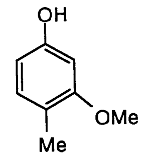
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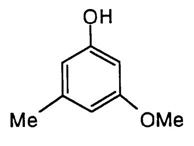
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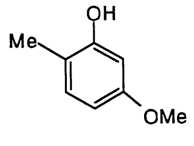
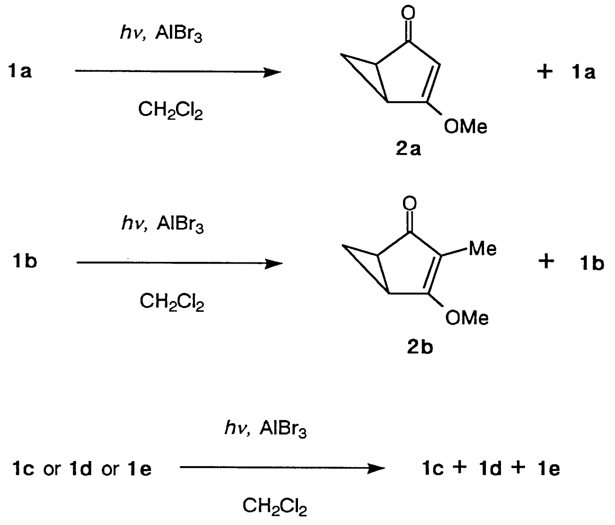

1e

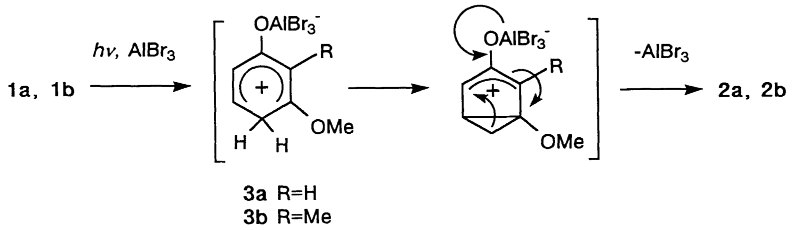
When a solution of **1a** and 2 equiv of AlBr$_3$ in CH$_2$Cl$_2$ was irradiated through a Pyrex filter, 4-methoxybicyclo[3.1.0]hex-3-en-2-one (**2a**) was obtained in a 38% isolated yield (74% yield based on **1a** consumed) along with unreacted **1a** (43% conversion).[4] The conversion of **1a** to **2a** reached maximum after about 4.5 h irradiation and by prolonged irradiation the relative ratio of **2a** decreased gradually due to photochemcal cycloreversion to **1a**. Similar cycloreversion of bicyclo[3.1.0]hex-3-en-2-ones has been reported.[5] Indeed, independent irradiation of **2a** showed that **2a** isomerized to **1a** efficiently irrespective of the presence of AlBr$_3$. While irradiation of **2a** in the presence of AlBr$_3$ (2 equiv) gave an equilibrium mixture of **2a** and **1a**, the cycloreversion of **2a** was irreversible in the absence of AlBr$_3$ to afford **1a** in a 83% yield.



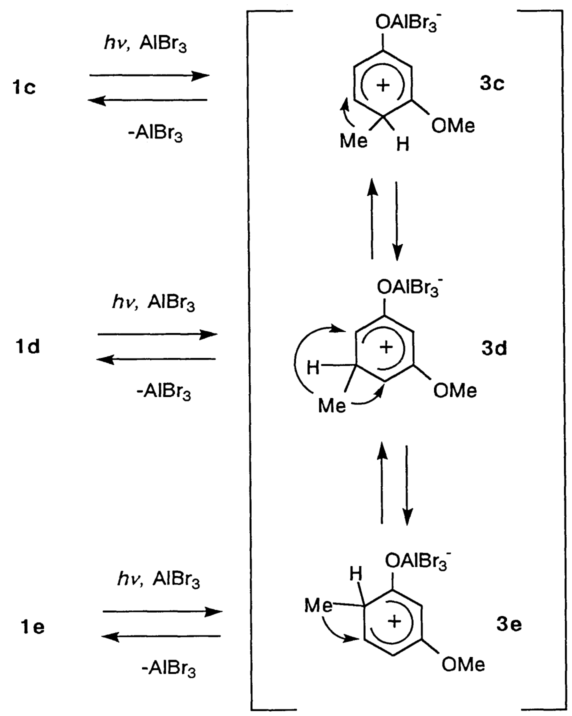
On the other hand, irradiation of the 4-methyl derivative **1c** with AlBr$_3$ (2 equiv) gave an equilibrium mixture composed of **1c**, 3-methoxy-5-methylphenol (**1d**), and 5-methoxy-2-methylphenol (**1e**)(**1c**:**1d**:**1e**= 24:36:39). Similarly, irradiation of **1d** and **1e** with AlBr$_3$ gave mixtures of **1c**, **1d**, and **1e** (7:34:59 from **1d**, 3:26:70 from **1e**). No bicyclohexenones were detected in these cases. It became apparent that the mode of isomerization, i.e., lumiketone-type rearrangement or methyl transposition, of the methyl derivatives **1b**—**1e** is critically dependent on the position of the methyl group.

The above reactivity difference is explained in terms of the reaction pathways shown in Scheme 1 and 2. In view of the previous work done by Childs,[1] it is reasonable to assume that the lumiketone-type rearrangement of **1a** and **1b** proceeds through the para protonated complexes **3a** and **3b**, respectively (Scheme 1). On the other hand, the methyl transposition of **1c**—**1e** is explained by positing the respective complexes **3c**—**3e** which are protonated on the methyl-bearing carbons of the phenol ring. These are interconverted by 1,2-migration of the methyl group, which is located adjacent to the carbocation centers (Scheme 2).

Although the lumiketone-type transformation was successful only for **1a** and **1b**, it should be pointed out



Scheme 1.



Scheme 2.

that products **2a** and **2b** possess a β-methoxy-α,β-enone functionality which is a versatile synthon for further functional group transformation. Moreover, although isolated yields of **2a** and **2b** were only moderate, the products were isolated in an almost pure state by simple extraction and the starting material can be recovered from the alkaline extract. Therefore, despite its limitations, the present transformation provides a useful way to prepare bicyclo[3.1.0]hex-3-en-2-one derivatives from readily available 3-methoxyphenols.

Experimental

IR spectra were recorded on a Hitachi 260-10 spectrometer. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured with a JEOL JNM-GSX-400 spectrometer. Mass spectra were obtained with a JEOL JMS-DX303 spectrometer. GLC was undertaken with Hitachi G-3000 chromatograph with a capillary column of FFAP (6 m).

3-Methoxyphenol (**1a**) was commercially available and was distilled before use. 3-Methoxy-2-methylphenol (**1b**),[6] 3-methoxy-4-methylphenol (**1c**),[7] 3-methoxy-5-methylphenol (**1d**),[8] and 5-methoxy-2-methylphenol (**1e**)[9] were prepared according to the reported procedures.

Photoisomerization of 3-Methoxyphenol (1a) to 2a. A solution of 500 mg (4.03 mmol) of **1a** and 2.15 g (8.06 mmol) of $\mathrm{AlBr_3}$ in 25 ml of $\mathrm{CH_2Cl_2}$ was irradiated with a 500 W high pressure mercury lamp through a Pyrex filter at room temperature. The progress of the reaction was monitored by GLC. After 4.5 h, the mixture was carefully added to ice water and extracted three times with ether. The ether extract was washed with 10% NaOH solution, brine, and dried with $\mathrm{MgSO_4}$. Evaporation of the solvent followed by chromatography on silica gel (elution with ether) gave 159 mg (38% yield; 74% based on consumed **1a**) of **2a**. The alkaline washing was acidified with HCl and extracted with ether. The extract was washed with brine, dried, and evaporated. Chromatography on silica gel (elution with 20% ether in petroleum ether) afforded 286 mg (57% recovery) of unreacted **1a**.

2a: IR (neat) 1680, 1580, 1240, and 960 cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$) δ=4.65 (s, 1H), 3.80 (s, 3H), 2.29 (m, 1H), 2.17 (m, 1H), and 1.4—1.5 (m, 2H); ^{13}C NMR ($\mathrm{CDCl_3}$) δ=203.3 (s), 191.2 (s), 95.7 (d), 58.8 (q), 31.4 (t), 24.2 (d), and 20.5 (d); MS m/z (rel intensity) 124 (M$^+$, 100), 96 (45), 81 (36), and 53 (57). Found: C, 67.62; H, 6.44%. Calcd for $\mathrm{C_7H_8O_2}$: 67.73; H, 6.50%.

Photoisomerization of 3-Methoxy-2-methylphenol (1b) to 2b. A solution of 100 mg (0.724 mmol) of **1b** and 386 mg (1.45 mmol) of $\mathrm{AlBr_3}$ in 5 ml of $\mathrm{CH_2Cl_2}$ was irradiated as above for 30 min. The reaction was worked up as above to give 19 mg (19% yield; 33% based on **1b** consumed) of **2b** and 42 mg (58% conversion) of unreacted **1b**.

2b: IR (neat) 1680, 1620, 1280, 1240, 1000, and 930 cm^{-1}; ^{1}H NMR ($\mathrm{CDCl_3}$) δ=3.98 (s, 3H), 2.28 (m, 1H), 2.12 (ddd, J=3.9, 6.8, and 8.3 Hz, 1H), 1.47 (ddd, J=3.9, 4.9, and 7.8 Hz, 1H), 1.44 (s, 3H), and 1.31 (dd, J=3.9 and 7.3 Hz, 1H); ^{13}C NMR ($\mathrm{CDCl_3}$) δ=203.4 (s), 185.1 (s), 108.2 (s), 57.0 (q), 33.1 (t), 23.1 (d), 16.1 (d), and 5.6 (q); MS m/z (rel intensity) 138 (M$^+$, 100), 107 (30), 95 (23), 79 (26), and 67 (35). HR MS Found: m/z 138.0678. Calcd for $\mathrm{C_8H_{10}O_2}$: M, 138.0681.

Photoisomerization of 3-Methoxy-4-methylphenol (1c), 3-Methoxy-5-methylphenol (1d), and 5-Methoxy-2-methylphenol (1e). Irradiation of 100 mg (0.75 mmol) of **1c** or **1d** or **1e** and 398 mg (1.5 mmol) of $\mathrm{AlBr_3}$ in 5 ml of $\mathrm{CH_2Cl_2}$ was undertaken as above for 10 h. The mixture was worked up as above and the subsequent flash chromatography on silica gel (ether–hexane=10 : 90 eluent) gave a mixture of **1c**, **1d**, and **1e**. Yields and the ratio of the products (GLC) are as follows: From **1c**: 71 mg (71% yield), **1c** : **1d** : **1e**=24 : 36 : 39. From **1d**: 71 mg (71% yield), **1c** : **1d** : **1e**=7 : 34 : 59. From **1e**: 61 mg (61% yield), **1c** : **1d** : **1e**=3 : 26 : 70. The products were identified by GLC and ^{1}H NMR spectra.

1c: ^{1}H NMR ($\mathrm{CDCl_3}$) δ=6.94 (d, J=8.3 Hz, 1H), 6.37 (s, 1H), 6.31 (d, J=8.3 Hz, 1H), 5.01 (s, 1H), 3.77 (s, 3H), and 2.12 (s, 3H).

1d: ^{1}H NMR ($\mathrm{CDCl_3}$) δ=6.31 (br s, 1H), 6.26 (br s, 1H), 6.23 (t, J=2.5 Hz, 1H), 5.59 (br s, 1H), 3.74 (s, 3H), and 2.25 (s, 3H).

1e: ^{1}H NMR (CDCl$_3$) δ=6.99 (d, J=8.3 Hz, 1H), 6.41 (dd, J=2.5 and 8.3 Hz, 1H), 6.38 (d, J=2.5 Hz, 1H), 5.28 (br s, 1H), 3.74 (s, 3H), and 2.16 (s, 3H).

Photocycloreversion of 4-Methoxybicyclo[3.1.0]hex-3-en-2-one (2a). A solution of 80 mg (0.65 mmol) of **2a** in 4 ml of CH$_2$Cl$_2$ was irradiated for 1 h until the starting material was consumed completely. The solvent was evaporated and the subsequent flash chromatography gave 66 mg (83% yield) of **1a**.

A solution of 80 mg (0.65 mmol) of **2a** and 344 mg (1.3 mmol) of AlBr$_3$ in 4 ml of CH$_2$Cl$_2$ was irradiated for 1 h. The mixture was worked up as described for the isomerization of **1a** to **2a**. After chromatography, 40 mg (50% yield) of **1a** and 19 mg (24% yield) of unreacted **2a** were obtained. By prolonged irradiation, while the ratio of **1a** and **2a** did not change appreciably, their yields decreased due to the formation of a small amount of unidentified side products.

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References

1) a) R. F. Childs, B. D. Parrington, and M. Zeya, *J. Org. Chem.*, **44**, 4912 (1979). b) P. Baeckstrom, U. Jacobsson, B. Koutek, and T. Norin, *ibid.*, **50**, 3728 (1985). c) S. K. Chadda and R. F. Childs, *Can. J. Chem.*, **63**, 3449 (1985). d) R. F. Childs and B. E. George, *ibid.*, **66**, 1343 (1988).

2) For reviews: P. J. Kropp, "Organic Photochemistry," ed by O. L. Chapman, Marcel Dekker, New York (1967), Vol. 1, p. 1; K. Schaffner and M. Demuth, "Rearrangements in Ground and Excited States," ed by P. de Mayo, Academic Press, New York (1980), Vol. 3, p. 281.

3) For a Lewis acid-mediated photoreaction of 2-naphthols: M. Ue, M. Kinugawa, K. Kakiuchi, Y. Tobe, and Y. Odaira, *Tetrahedron Lett.*, **30**, 6193 (1989).

4) Although it has been reported that similar photoisomerization of methyl-substituted phenols is dependent on the irradiation wavelength,[1a)] irradiation of **1a** through a solution filter of 1,4-diphenylbutadiene in tetrahydrofuran (0.15 mol dm^{-3}; λ>350 nm) resulted in essentially the same results as that from irradiation through a Pyrex filter. Moreover, CF$_3$SO$_3$H[1b,c)] was found to be uneffective for this transformation.

5) J. W. Wheeler and R. H. Eastman, *J. Am. Chem. Soc.*, **81**, 2361 (1959); H. E. Zimmerman, R. Keese, J. Nasielski, and J. S. Swenton, *ibid.*, **88**, 4895 (1966); L. Barber, O. L. Chapman, and J. D. Lassila, *ibid.*, **90**, 5933 (1968).

6) A. Rashid and G. Read, *J. Chem. Soc. C*, **1967**, 1323.

7) R. N. Mirrington and G. I. Feutrill, *Org. Synth.*, **53**, 90 (1973).

8) M. Tomita and S. Ueda, *Yakugaku Zasshi*, **80**, 353 (1960).

9) J. Wu, J. L. Beal, and R. W. Doskotch, *J. Org. Chem.*, **45**, 208 (1980).