CHEMISTRY LETTERS, pp. 1931-1934, 1987.

Direct Formations of o-Tropoquinone Bisacetals from 2,3- and 2,7-Dimethoxytropones and p-Tropoquinone Bisacetals from 2-Bromo-7-methoxytropone by the Anodic Oxidation

Akira MORI,\* Tadahiko KUBOTA,<sup>†</sup> Seishi KASAI,<sup>†</sup> and Hitoshi TAKESHITA\* Institute of Advanced Material Study, 86, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816 <sup>†</sup>Graduate School of Engineering Sciences, 39, Kyushu University, Kasuga-koen, Kasuga, Fukuoka 816

Anodic oxidation of 2,7- and 2,3-dimethoxytropones gave the correspondong isomeric o-tropoquinone bisacetals, 2,2,7,7-tetrame-thoxycyclohepta-3,5-dienone and 2,2,3,3-tetramethoxycyclohepta-4,6-dienone in good yields. By  $H_2SO_4$ -treatment in AcOH-Ac<sub>2</sub>O, former afforded 4-acetoxy-2,7-dimethoxytropone, 2,5-diacetoxy-7-methoxytropone and 4,5-diacetoxy-3-methoxytropone, latter did no such product. Similar oxidation of 2-bromo-7-methoxytropone gave alternative p-tropoquinone bisacetal derivatives.

Recently, we have prepared<sup>1-3)</sup> the p-tropoquinone acetals from 5-hydroxytropolone derivatives and noteworthy are their characteristic photochemical behaviors; e.g., the 2,2-dialkoxy-3,6-cycloheptadiene-1,5-diones isomerized to alkyl 2,5-dioxo-3-cyclopentenylacetates ( $\mathbf{A}$ ),<sup>1)</sup> and internally acetalized 5-alkyl-1-hydroxy-8-oxabicyclo[3.2.1]octa-3,6-dien-2-ones to 2-alkyl-3-oxatricyclo[3.3.0.0<sup>2,8</sup>]octane-4,6-diones ( $\mathbf{B}$ ).<sup>3)</sup> Since  $\mathbf{A}$  and  $\mathbf{B}$  have a utility in organic syntheses, a direct method of preparation is desirable. Moreover, there has been no report on the preparation of o-tropoquinone acetal. Herein, we will describe a convenient preparation of o- and p-tropoquinone acetals from alkoxytropones by means of anodic oxidation. Benzoquinone mono-acetal was prepared from p-methoxyphenol using this method.<sup>4)</sup>

When 2,7-dimethoxytropone ( 1 ) and 2,3-dimethoxytropone ( 2 ) were oxidized anodically in anhydrous MeOH in the presence of  ${\rm LiCl0}_4, ^{5)}$  o-tropoquinone bis-

acetals (  $\bf 3$  and  $\bf 4$  ) were obtained in 94% and 60% yields, respectively, together with a dimeric product (  $\bf 5$  ) of  $\bf 4$  in 6% yield.



Their structures were determined from the NMR spectra. Since **3** [  $\delta(H)^{6}$ =3.26 (12H, s), 5.5-5.7(2H, m), and 6.1-6.3(2H, m).  $\delta(C)$ =50.5(4C), 101.0(2C), 127.4(2C), 130.2(2C), and 192.5] and **4** [  $\delta(H)$ =3.36(6H, s), 3.42(6H, s), 5.86(1H, dd, J=12, 1 Hz), 6.06(2H, m), and 6.40(1H, ddd, J=12, 6, 2 Hz).  $\delta(C)$ =51.3(2C), 52.9(2C), 101.2, 103.5, 126.2, 128.1, 133.4, 137.9, and 194.5] had four methoxyl groups and four olefinic protons, **3**, having a symmetrical element, is 2,2,7,7-tetramethoxycyclohepta-3,5-dienone and **4** is 2,2,3,3-tetramethoxycyclohepta-4,6-dienone. The NMR spectra of **5** [  $\delta(H)$ =2.26(2H, d, J=11 Hz), 2.62(2H, m), 2.96(2H, t, J=11 Hz), 3.17 (6H, s), 3.35(6H, s), 3.38(6H, s), 3.47(6H, s), 5.73(2H, dd, J=11.7, 2.2 Hz), and 5.93(2H, dd, J=11.7, 3.7 Hz).  $\delta(C)$ =39.1(2C), 44.8(2C), 50.6(2C), 51.1(2C), 51.2 (2C), 51.5(2C), 101.6(2C), 106.2(2C), 132.1(2C), 134.3(2C), and 202.7(2C)] again suggested its structure to be bi(4,4,5,5-tetramethoxy-6-oxocyclohept-2-enyl).

The anodic oxidation of 2-bromo-7-methoxytropone (**6**) afforded p-tropoquinone tetramethyl bisacetal (**7** [  $\delta$ (H)=3.29(6H, s), 3.30(6H, s), 5.82(1H, d, J=12.5 Hz), 6.01(1H, d, J=12.5 Hz), 6.09(1H, dd, J=12.5, 2 Hz), and 6.34(1H, dd, J=12.5, 2 Hz).  $\delta$ (C)=49.7(2C), 50.4(2C), 98.5, 101.9, 127.4, 131.2, 135.9, 139.8, and 193.0] ) and

its 2-bromo derivative (**8** [ $\delta$ (H)=3.24(6H, s), 3.27(6H, s), 5.82(1H, d, J=12 Hz), 6.07(1H, dd, J=12, 2 Hz), and 6.84(1H, d, J=2 Hz).  $\delta$ (C)=49.8(2C), 50.6(2C), 99.4, 101.0, 121.2, 131.0, 135.5, 140.1, and 188.3]) in 22% and 67% yields.<sup>7)</sup> The former was also prepared from the anodic oxidation of 2,5-dimethoxytropone (**9**) quantitatively. The formation of **7** from **6** is different to the change of **1** to **3** and can be explained in terms of poor spin density at the brominated carbon in the intermediary-formed pentadienyl radical ( or pentadienyl cation ) species. Moreover, we extended this oxidation to 2-alkoxy-5-hydroxytropones (**10** and **11**) to prepare p-tropoquinone dimethyl acetal (**12**), in 62% yield, and a bisacetal (**13**), in 75% yield, which were identical with authentic samples.<sup>2</sup>) Interestingly, this electrode oxidation and cerium(IV) ammonium nitrate ( CAN )-oxidation<sup>8</sup>) were complemental to some extent; **1** having shown better results in the present electrode oxidation was inert towards CAN to cause only 7% conversion to **3** after 4.5 h, while the CAN-oxidation of **2** instantly gave **4** in quantitative yield.



Next,  $H_2SO_4$ -treatment in AcOH-Ac<sub>2</sub>O of **3** gave three products (14 [  $\delta$ (H)=2.32 (3H, s), 3.93(6H, s), 6.62(1H, d, J=2.6 Hz), 6.65(1H, dd, J=10.3, 2.6 Hz), and 6.80 (1H, d, J=10.3 Hz).  $\delta$ (C)=21.1, 56.6(2C), 111.6, 112.2, 117.3, 147.8, 160.6, 161.2, 169.5, and 173.1], 15 [  $\delta$ (H)=2.33(3H, s), 2.36(3H, s), 3.94(3H, s), and 6.59(1H, d, J=2.2 Hz), 6.62(1H, dd, J=10.3, 2.2 Hz), and 7.24(1H, d, J=10.3 Hz)], and 16 [  $\delta$ (H)=2.29(6H, s), 3.80(3H, s), 6.51(1H, d, J=2.2 Hz), 6.78(1H, d, J=12.8 Hz), and 6.91 (1H, dd, J=12.8, 2.2 Hz)]) in 41%, 13%, and 6% yields, respectively. Similar treatment of **4** afforded the hydrolysis products (17 [  $\delta$ (H)=3.38(6H, s), 6.0-6.1(2H, m), and 6.5-6.6(2H, m).  $\delta$ (C)=52.7(2C), 104.6, 129.5 (2C), 133.0(2C), and 195.1(2C)]) and 2-acetoxyanisole (18)<sup>9</sup> in 46% and 22% yields without any Thiele-type product. From the <sup>1</sup>H NMR spectrum showing two methoxyl signals, an acetoxyl signal, and three olefinic protons, a singlet and an AB-type signals, the structure of 14 was deduced to be 4-acetoxy-2,7-dimethoxytropone. On the other hand, 15 and 16 showed

a methoxyl signal, two acetoxyl groups, and three olefinic protons, respectively. Furthermore, a long-range coupling between the methoxyl group and the isolated aromatic proton was observed in 15 and 16. From the coupling constant of AB-type signals (10.3 Hz for 15 and 12.8 Hz for 16), the structures of 15 and 16 were 2,5-diacetoxy-7-methoxytropone and 4,5-diacetoxy-3-methoxytropone. Thus, behaviors of **3** and **4** toward  $H_2SO_4$ -treatment are quite different.<sup>10</sup>

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- 5) A typical procedure of anodic oxidation is as follows: An anhydrous MeOH solution ( $50 \text{ cm}^3$ ) of 1 (48.2 mg) and  $\text{LiClO}_4$  (54 mg) was electrolyzed in an undivided cell fitted with circular Pt-gauze (10 mm in diameter x 20 mm in height)-anode and a Pt cathode under a constant current. After 3.1 F/mol of electricity were passed at room temperature under N<sub>2</sub> atmosphere, the solvent was evaporated in vacuo. The residue was diluted with water and extracted with CHCl<sub>3</sub>. The solvent was evaporated and the residue was chromatographed on a silica-gel column to give **3** (62.1 mg; 94%).
- 6) The NMR spectra were measured in  $\text{CDCl}_3$  by means of a JEOL FX-100 or GSX 270 Model Spectrometer.
- 7) It should be noted that the yield of 7 from 2-methoxytropone by electrode oxidation was less satisfactory (49%) than the total yield of 7 and 8 in the present case (89%). Moreover, further electrolysis of 8 with 2 F/mol did not produce 7 at all. Therefore, 8 is not a precursor of 7. As a result, 7 must be formed via 2e-oxidation followed by allylic displacement of bromide by methoxide ion. Detailed discussion will be made in a full paper.
- 8) A. Mori, Y. Isayama, and H. Takeshita, Bull. Chem. Soc. Jpn., 59, 511 (1986).
- 9) A novel ring contraction to lead **18** could be explained by a modified benzilic acid rearrangement of **17** followed by decarboxylation.
- 10) We wish to thank The Ministry of Education, Science, and Culture for a financial assistance, Grant-in-Aid for Scientific Research to A. M. ( No. 60470025 ).

( Received July 10, 1987 )