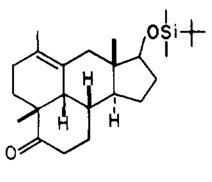

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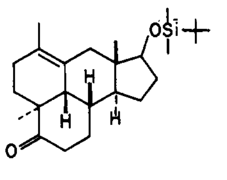
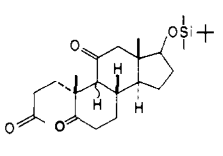


12

13, 85% yield; NMR δ 0.76, 1.1 (quaternary CH_3's), 2.09 (CH_3CO). It is clear that the triketone **13** can, in principle, cyclize to the acylcyclopentanol **14**. The latter is indeed the kinetic product obtained, quantitatively [NMR δ 0.86, 1.30, 2.16 (CH_3CO)], upon treatment with 4% methanolic potassium hydroxide (room temperature, nitrogen, 5 min). The dehydration of **14** is, fortunately, relatively slow, and the intermediate ketol **14**, or the starting triketone **13**, is converted by warming it to 40 °C (nitrogen, 30 min) in 85–90% yield to the 11-ketotestosterone **15** identical with the material made by silylation of authentic[7] 11-ketotestosterone.



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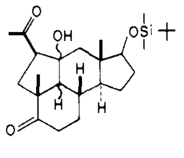

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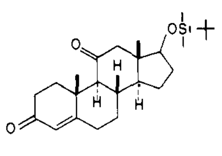

15

The efficiency of this construction of an 11-ketosteroid system from the hydrindanone **7** has led us to seek novel and efficient processes for the synthesis of such hydrindanones. We will report shortly on this phase of our work.

Acknowledgment. We thank the National Institutes of Health and the National Science Foundation for their support of this work.

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Photosensitized Oxygenation of α-Diazoquinone

Wataru Ando* and Hajime Miyazaki

Department of Chemistry, The University of Tsukuba
Sakura-mura, Ibaraki 305, Japan

Katsuhiko Ueno and Hachiro Nakanishi

Research Institute for Polymers and Textiles
Yatabe-cho, Ibaraki 305, Japan

Tosio Sakurai and Kimiko Kobayashi

Institute of Physical and Chemical Research
Wako-shi, Saitama 351, Japan

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The activation of molecular oxygen catalyzed by dioxygenases by which an oxygen molecule is incorporated into a substrate has received much attention in biological and chemical studies.[1-5]

Several reactions have been reported as nonenzymic models for the enzymatic hydroxylation[6-9] and cleavage of aromatic compounds by oxygenases.[10,11] Catechol is oxidized to muconic acid derivatives by singlet oxygen,[12] superoxide,[13] and molecular oxygen activated with cuprous chloride.[14] Some of these cleavage reactions are rationalized by assuming hydroperoxy hemiketal **1** or α-carbonyl carbonyl oxide **2** as a possible intermediate of enzymic model oxidations.[15]

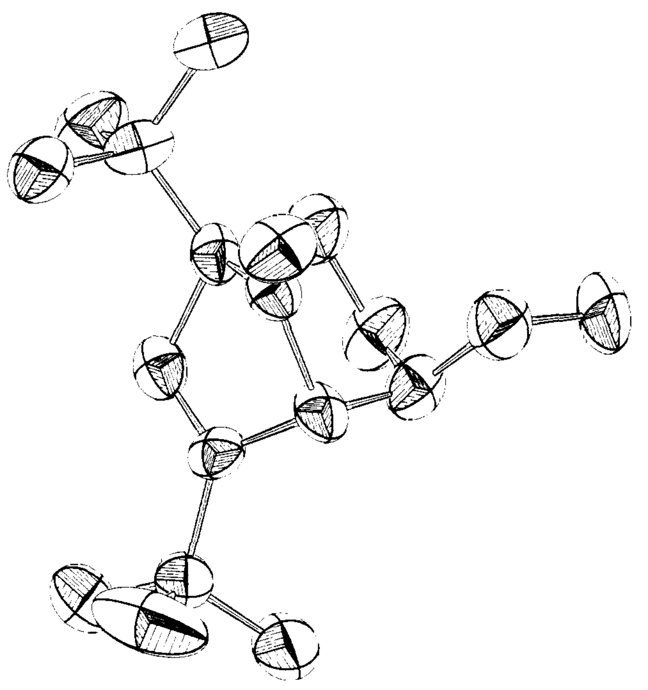
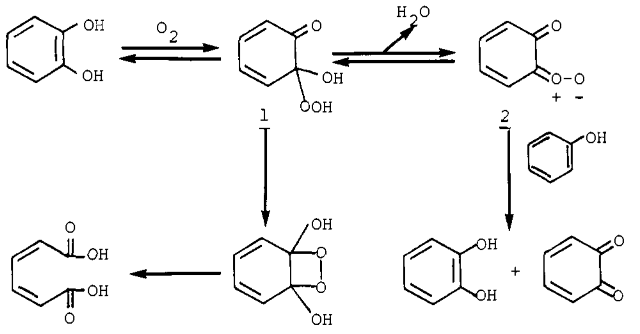
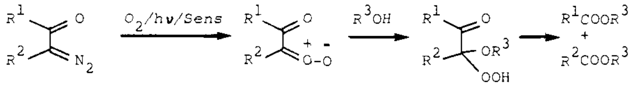


Figure 1. Perspective view of the cyclic peroxide **5**.



Recently, we observed that the reaction of singlet oxygen with α-diazo ketone gave the products derived from α-keto hydroperoxide and 1,2-dioxetane via α-carbonyl carbonyl oxide.[16-18]



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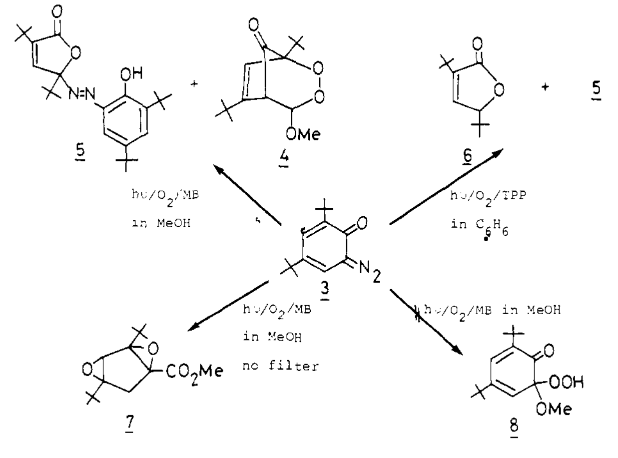
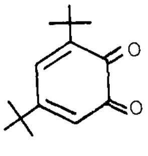
Now, in the hope of the direct generation of α-carbonyl carbonyl oxide **2** or the hydroperoxy hemiketal **1** in nonenzymic oxidation of catechol and *o*-benzoquinone, we studied the photosensitized oxygenation of 4,6-di-*tert*-butyl-2-diazo-1,2-benzoquinone (**3**) and isolated the unusual bicyclic carbonyl peroxide in high yield.

Methanol solution of α-diazoquinone **3**[19] (2.0 g, 8.8 mmol) with methylene blue as a sensitizer was irradiated with a Na lamp for 12 h under oxygen bubbling. Evaporation followed by silica gel chromatography gave two main products, the cyclic peroxide **4** (mp 109–110 °C dec, positive peroxide test by KI/AcOH) and azofuranone **5**[20] in 60 and 15% yields, respectively. The formation of 3,5-di-*tert*-butyl-1,2-benzoquinone (**9**) and muconic acid derivative **10** expected from the nonenzymic oxidation of catechol[12-14] could not be observed upon analysis of the NMR spectrum of the reaction mixture. The structural assignment of **4** is based on the following spectral data: ^{1}H NMR (CCl_4, Me_4Si) δ 1.05 (s, 9 H), 1.17 (s, 9 H), 2.09 (d, J = 3.0 Hz, 1 H), 3.43 (s, 3 H), 4.97 (d, J = 3.0 Hz, 1 H), 6.06 (s, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 24.71 (q), 27.96 (q), 33.38 (s), 34.08 (s), 54.99 (d), 55.64 (q), 96.01 (s), 107.28 (d), 121.32 (d), 159.29 (s), 195.21 (s); IR (KBr) 2950, 1760, 1100 cm^{-1}; mass spectrum, *m/e* 208 ($M^+ - COOCH_3$). Anal. Calcd for $C_{15}H_{24}O_4$: C, 67.13; H, 9.01. Found: C, 67.19; H, 9.03. X-ray crystal analysis established the exact structure of the peroxide **4** which is shown in Figure 1. The cyclic peroxide **4** could not be reduced by trimethyl phosphite. On thermolysis at 80 °C in benzene, cyclopentadienone epoxide (**11**), 4,6-di-*tert*-butyl-2-pyrone (**12**), and methyl formate were formed in yields of 25, 75, and 67%, respectively, as confirmed by NMR and analytical data.[21] Control experiments monitored by NMR spectroscopy showed that the epoxide **11** and methyl formate were initial decomposition products and then 2-pyrone **12** was formed.[22] Photosensitized oxygenation of α-diazoquinone **3** in benzene at 25 °C was also carried out under the same conditions. 3,5-Di-*tert*-butyl-2-furanone (**6**)[23] was obtained as a major product in 87% yield, together with the azofuranone **5** in 13% yield. On the other hand, photosensitized oxygenation of **3** in methanol using a halogen lamp (no filter) resulted in the formation of the epoxide **7**[25] in 57% yield. Wolff rearrangement is a favorable process under the conditions.

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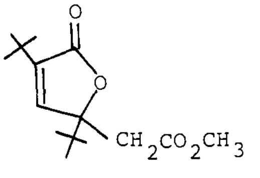
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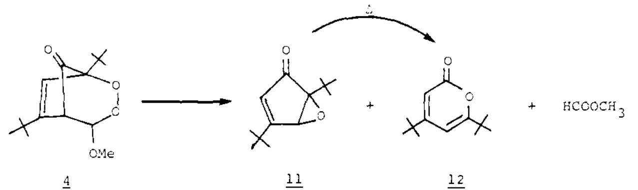

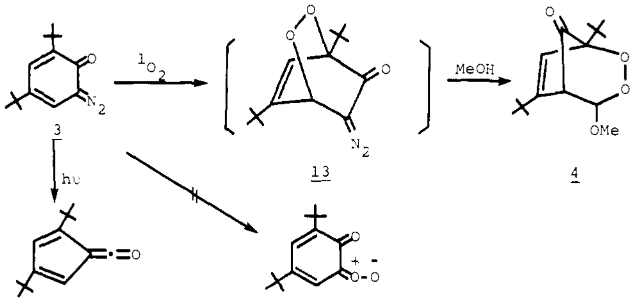

On the basis of the above results, an attractive mechanism for the formation of cyclic peroxide **4** may involve the formation of the endoperoxide[26] **13** followed by unusual rearrangement with methanolysis. Under these conditions, the diazo group may not be attacked by singlet oxygen. Therefore, the hydroperoxy hemiketal **8** or α-carbonyl carbonyl oxide were not formed in this reaction. However, the unique reaction of α-diazoquinone with singlet oxygen was found. The azofuranone may be formed by the coupling reaction of the furanone **6** and unreacted diazoquinone **3**.[28]

Further investigation on enzymic oxidation is now in progress.

Acknowledgment. We thank Dr. Takahiro Tezuka for his helpful discussions and suggestions.

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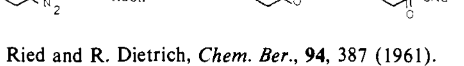
(18) Photosensitized oxygenation of 2-diazocyclohexanone in methanol afforded dimethyl adipate and 1,2-cyclohexadione in 60 and 25% yield, respectively.



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(20) Orange crystals, mp 144–145 °C; ^{1}H NMR ($CDCl_3$, Me_4Si) δ 12.23 (s, 1 H), 7.70 (d, J = 2.7 Hz, 1 H), 7.47 (d, J = 2.7 Hz, 1 H), 7.23 (s, 1 H), 1.43 (s, 9 H), 1.37 (s, 9 H), 1.28 (s, 9 H), 1.17 (s, 9 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 25.01 (q), 28.18 (q), 29.45 (q), 31.35 (q), 31.94 (s), 34.28 (s), 35.30 (s), 38.47 (s), 106.39 (s), 127.11 (d), 129.11 (d), 135.98 (s), 137.93 (s), 141.49 (s), 142.76 (d), 144.91 (s), 149.64 (s), 169.77 (s); IR (CCl_4) 3520, 3420, 2950, 1760, 1600 cm^{-1}. Anal. Calcd for $C_{26}H_{40}N_2O_3$: C, 72.86; H, 9.41; N 6.54. Found: C, 72.86; H, 9.47; N, 6.52.

(21) Cyclopentadienone epoxide (**11**): ^{1}H NMR (CCl_4, Me_4Si) δ 1.10 (s, 9 H), 1.23 (s, 9 H), 3.78 (d, J = 3.0 Hz, 1 H), 5.50 (d, J = 3.0 Hz, 1 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 25.79 (q), 28.01 (q), 29.69 (s), 34.45 (s), 57.15 (d), 66.42 (s), 125.36 (d), 180.46 (s), 200.34 (s); IR (CCl_4) 1710 cm^{-1}. Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.67. Found: C 74.98; H, 9.69. 2-Pyrone (**12**): ^{1}H NMR (CCl_4, Me_4Si) δ 1.27 (s, 9 H), 1.33 (s, 9 H), 5.97 (m, 2 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ, 28.06 (q), 28.98 (q), 35.32 (s), 36.08 (s), 98.60 (d), 107.16 (d), 163.99 (s), 167.78 (s), 171.41 (s); IR (CCl_4) 1720 cm^{-1}. Anal. Calcd for $C_{13}H_{20}O_2$: C, 74.96; H, 9.67. Found: C, 74.42; H, 9.72.

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(23) ^{1}H NMR (CCl_4, Me_4Si) δ 0.96 (s, 9 H), 1.26 (s, 9 H), 4.48 (d, J = 3.5 Hz, 1 H), 6.92 (d, J = 3.5 Hz. 1 H); IR (CCl_4) 1740 cm^{-1}. The structure of the furanone was determined in comparison with an authentic sample prepared by the method of Wiberg et al.[24]

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(25) ^{1}H NMR (CCl_4, Me_4Si) δ 0.93 (s, 9 H), 1.03 (s, 9 H), 2.01 (q, J = 15 Hz, 2 H), 3.19 (s, 1 H), 3.63 (s, 3 H); ^{13}C NMR ($CDCl_3$, Me_4Si) δ 32.1 (s), 32.5 (s), 25.9 (q), 26.0 (q) 29.6 (t), 52.0 (q), 55.9 (d), 72.2 (s), 74.7 (s), 79.1 (s), 167.7 (s); IR (CCl_4) 1720 cm^{-1}. Anal. Calcd for $C_{15}H_{24}O_4$: C, 67.13; H. 9.01. Found: C, 66.80; H, 8.76.

(26) Foote et al. have isolated this endoperoxide from photooxygenation of **3** in CH_2Cl_2 at −78 °C.[27]

(27) We thank Professor Foote for a prepublication copy of his manuscript: H.-S. Ryang and C. S. Foote, *J. Am. Chem. Soc.*, following paper in this issue.

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