

STRUCTURES OF THE NOVEL DIMERS OF 1-ALKOXY-2-BENZOPYRYLIUM-4-OLATES

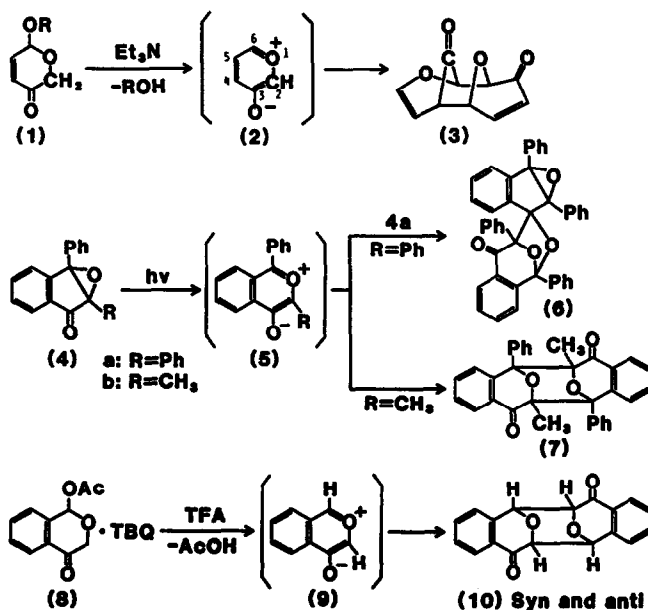
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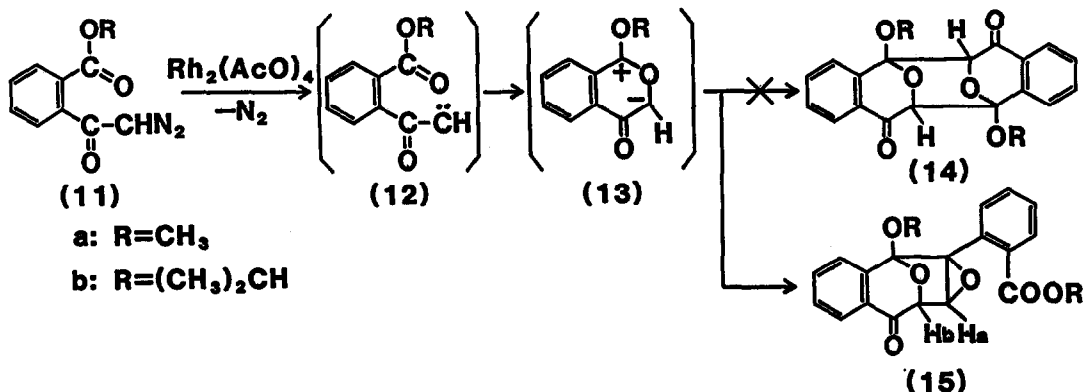
Summary: The structure of novel type dimers of 1-methoxy- and 1-isopropoxy-2-benzopyrylium-4-olates was determined by spectroscopic and single-crystal X-ray structural analyses to have 4-alkoxy-5-(*o*-alkoxycarbonylphenyl)-4,7;5,6-bisepoxy-2-benzocycloheptan-1-ones.

The chemistry of carbonyl ylide has attracted interest of organic chemists from theoretical and synthetic stand points.^{1,2)} Various methods to generate carbonyl ylides have been studied; photolysis of epoxide,¹⁾ carbene-carbonyl reaction,³⁾ thermolysis of Δ^3 -1,3,4-oxadiazoline.⁴⁾ Pyrylium-3-olate (2) and 2-benzopyrylium-4-olates (5 and 9) have the carbonyl ylide resonance structures and exert 1,3-dipolar cycloaddition toward ethylenic, acetylenic, and carbonyl compounds.⁵⁻⁷⁾ However, in the absence of these dipolarophiles, dimerization of the carbonyl ylides has been observed. For example, pyrylium-3-olate (2) produced by base catalyzed elimination of ROH from (1) gave a syn-(2,4;2,6) dimer (3).⁸⁾



Other types of dimers were reported for the 2-benzopyrylium-4-olates. Ullman and Milks have reported that 1,5-diphenyl-2-benzopyrylium-4-olate (5a) generated by the UV photolysis of 2,3-diphenyl-2,3-epoxyindanone (4a) gave a dimer (6) which was explained by the 1,3-dipolar cycloaddition of 5 toward the carbonyl group of the unphotolyzed 4a.⁹⁾ On the other hand, Zimmerman and Simkin reported the formation of a head-to-tail dimer (7) of 1-phenyl-5-methyl-2-benzopyrylium-4-olate (5b) in the photolysis of 2-methyl-3-phenyl-2,3-epoxyindanone (4b).⁶⁾ Similarly, Nilsen and Undenheim reported the formation of syn and anti head-to-tail dimers (10) of unsubstituted benzopyryliumolate (9) in the trifluoroacetic acid catalyzed reaction of 4-acetoxyisochromanone-TBQ adduct (8).¹⁰⁾

In a previous paper of this series the authors developed the novel method of the formation of carbonyl ylide by the electrophilic attack of carbene (or carbenoide) to the oxygen atom of carbonyl compounds,¹¹⁾ and generated 1-methoxy-2-benzopyrylium-4-olate (13) via intramolecular carbene-carbonyl reaction of ketocarbene (12) in the $\text{Cu}(\text{acac})_2$ catalyzed decomposition of *o*-methoxycarbonyl- α -diazoacetophenone (11a).^{7, 12)} We have tentatively assigned an anti head-to-tail structure (14) for the dimer obtained.¹²⁾ However, the detailed investigation of the spectroscopic data of the dimer revealed that the structure 14 is not correct. Therefore, we report here results of reinvestigation on the structure of the dimer of 13.



The $\text{Rh}_2(\text{OAc})_4$ -catalyzed decomposition of *o*-methoxycarbonyl- α -diazoacetophenone (11a) in absolute benzene using high dilution method gave a white crystalline product together with small amount of polymeric products. The results of elemental analysis and spectroscopic data suggest that the product is not the previously reported head-to-tail dimer (14a) but a dimer (15a) having 2-benzocycloheptan-1-one-4,7;5,6-bisepoxide structure [75 % yield; mp 152.8-153.4°C; IR (KBr) 1724 (ester C=O), 1708 (C=O), 1600, 1268, 755 cm^{-1} ; ¹H-NMR (CDCl₃) δ 3.40 (s, OCH₃), 3.64 (s, OCH₃), 4.34 (d, Ha, J=0.5 Hz), 4.88 (d, Hb, J=0.5 Hz), 6.92 (dd, 1H, arom-H, J=0.8, J=6.7 Hz), 7.35-7.64 (m, 6H, arom-H), 8.03 (dd, 1H, arom-H, J=1.2, J=6.7 Hz); ¹³C-NMR δ 51.90 (q, OCH₃),

53.00 (q, OCH₃), 59.51 (dd, Ca, J=4.2, J=201.1 Hz), 66.09 (s), 80.27 (dd, Cb, J=11.1, J=163.7 Hz), 104.49 (s), 124.71-140.25 (12 signals, arom-C), 166.63 (s, ester C=O), and 192.02 (s, C=O); MS, m/e 352 (M⁺)].¹³⁾

When small amount of solvent was used, side reactions occurred to form a large amount of tarry polymeric materials at the expense of yield of the dimer. Copper acetylacetonate is also effective for the decomposition of 11a to give the dimer.¹²⁾

o-Isopropoxycarbonyl- α -diazoacetophenone (11b) also gave the same type of dimer (15b) in 62 % yield in similar reaction conditions [¹H-NMR (CDCl₃) δ 1.18 (d, CH₃), 1.35 (d, CH₃), 4.27 (s, Ha), 4.82 (s, Hb), 4.3-5.0 (m, 2 CH of ⁱPr-), 6.80-7.00 (m, 1H, arom-H), 7.25-8.04 (m, 7H, arom-H)].

In order to confirm the structure of the dimer (15a), single crystal X-ray crystallography was performed on 15a recrystallized from benzene-hexane solution. The crystal structure was solved by the direct method (MULTAN-84) on 3002 reflections ($|F_o| > 1 \sigma(F_o)$) measured by a Rigaku four-circle diffractometer with graphite-filtered Mo-K α radiation using mixed scan method. As the ORTEP view shows (Fig. 1), the dimer has the 2-benzocycloheptan-1-one-4,7;5,6-bisepoxide structure (15a).¹⁴⁾

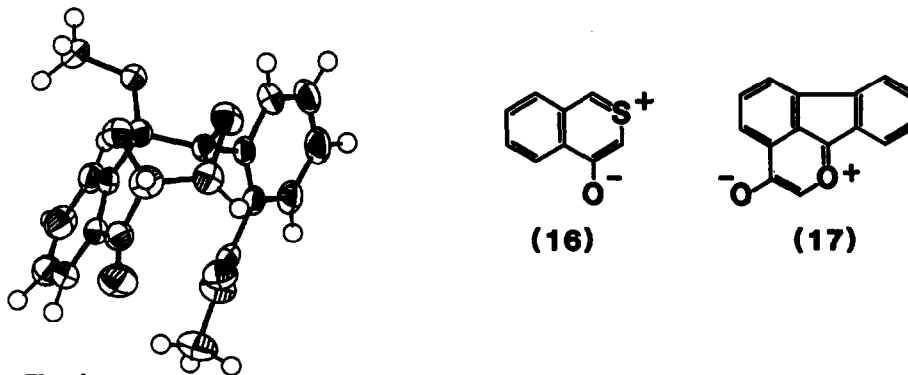


Fig. 1

In this way we had very interesting results that the structures of 2-benzopyrylium-4-olate dimers are strongly affected by the substituents (H, CH₃, Ph, and OCH₃) on C₁ and C₅ of 2-benzopyrylium-4-olates. Sulfur analogue (16) of benzopyrylium-4-olate gave a head-to-tail dimer.¹⁵⁾ Pyrylium-3-olate condensed with a fluorene ring (17) gave a head-to-head type dimer.¹⁶⁾ The experiments to determine the effect of substituents on the structure of dimers and to clarify the mechanism of the reaction are now under progress.

Procedure for the Decomposition of (11). A benzene solution (250 ml) of 11 (3 mmol) was added drop by drop into a stirred benzene solution (450 ml) of catalytic amount (5 mg) of Rh₂(OAc)₄ under reflux at 80°C in N₂ atmosphere. After the addition had been completed, the reaction mixture was heated until no more N₂ was evolved (about an hour). Solvent was evaporated under reduced pressure, and then the residue was chromatographed on silica gel using benzene-hexane as an eluent and recrystallized from benzene-hexane.

References and Footnotes

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- 13) The coupling constant between Ha and Hb ($J=0.5$ Hz) suggests the possibility of the bonding between the carbons having Ha and Hb on them as shown in structure **15**. The presence of two carbonyl carbon signals in ^{13}C NMR and the large coupling ($J=201.1$ Hz) of Ca indicating large sp^2 character corresponding to epoxide carbon could infer the structure **15**.
- 14) Crystal data of dimer (**15a**): $\text{C}_{20}\text{H}_{16}\text{O}_6$, $M_w=352.34$, monoclinic, space group $P2_1/c$, $a=8.118(2)$, $b=24.779(5)$, $c=9.028(2)$ Å, $\beta=114.46(1)$, $V=1653.0$ Å³, $Z=4$, $D_m=1.418$ g/cm³, $D_x=1.416$ g/cm³. The non-hydrogen atoms were refined anisotropically and hydrogen atoms isotropically to give $R=0.060$. Atomic co-ordinate, bond lengths and angles, and thermal parameters will be deposited at the Cambridge Crystallographic Data Center.
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(Received in Japan 28 August 1987)