Communications to the Editor

Chem. Pharm. Bull.
31(9)3357—3359(1983)

SPIROLACTONE OF XANTHENE (I)

A NOVEL PRODUCT FROM THE REACTION OF α-NAPHTHOL WITH OXALIC ACID

Michio Kimura* and Ichizo Okabayashi

Niigata College of Pharmacy
5829 Kamishin'ei-cho, Niigata 950-21, Japan

The condensation of α-naphthol with oxalic and sulfuric acids gives the novel compound, spiro[7H-dibenzo[c,h]xanthene-7,1'(2'H)-naphtho[1,2-b]furan]-2'-one, whose molecular structure was determined by X-ray diffraction methods.

KEYWORDS — spirolactone; spiro[7H-dibenzo[c,h]xanthene-7,1'(2'H)-naphtho[1,2-b]furan]-2'-one; α-naphthol; oxalic acid; X-ray analysis

In the course[1,2,3)] of an investigation of the reactivity of xanthene, we found that the condensation of α-naphthol with oxalic and sulfuric acids gave the novel spirolactone (III) of dibenzo[c,h]xanthene in excellent yield (70-75%) as shown in Chart 1. The condensation reaction was carried out by treating 7 g of α-naphthol with 3.5 g of oxalic acid and 2.5 ml of sulfuric acid at 135-140 °C. The resulting product from the condensation was purified by column chromatography on silica gel using a chloroform eluent, and recrystallization from xylene afforded brown crystals (mp 297 °C) of III. The elemental analysis of III gave the following results; Found(Calcd) for $C_{32}H_{18}O_3$: C 85.21(85.29), H 4.28(4.03) %. The mass spectrum showed only three key peaks, at m/z: 450(M^+), 422(M^+-CO), and 405(M^+-CO-OH). The infrared spectrum (KBr) revealed two chracteristic maxima: 1790 s(C=O), and 1642 w(C=C) cm^{-1}. The NMR spectrum in the $CDCl_3$ solution showed only multiple aromatic protons at the region from δ 6.6 to 9.0. However, the molecular structure of III, mainly based on chemical and spectroscopic data, has not been well established.

We now report the crystal and molecular structure of III determined by the X-ray diffraction method (Cu Kα radiation). Suitable crystals for X-ray investigation were obtained from a nitrobenzene solution as a 1:1 molecular complex[4)] of III and nitrobenzene. Space group $P\bar{1}$, a=11.296(1), b=13.050(2), c=11.138(1) Å α=113.43(1), β=94.18(1), γ=107.95(1)°, Z=4, V=1396.8 $Å^3$ and Dc=1.36 gcm^{-3}. The structure was solved by direct methods using MULTAN78[5)] and the block diagonal least-squares refinement gave R=0.049 and Rw=0.050. The established structure of III is given in the ORTEP drawing of Fig. 1. Compound III possesses a Ψ-like shape composed of three naphthalene rings of fused spirolactone, the most interesting point of which may be the dihedral angles of the naphthalene planes; 5.9° between ring A and B, 86.9° between ring A and C, and 81.4° between ring B and C, respectively. The average of the aromatic C-C bond distances in ring A, B and C are 1.397, 1.398 and 1.397 Å, respectively, while the average values of the

C-C-C angles are 120.0° for each of ring A, B, and C. The nitrobenzene molecules are packed by van der Waals forces (the intermolecular distances less than 3.275 Å) in the unit cell, and its benzene ring is almost parallel to ring C.

The established structure of III explains the novel reaction of α-naphthol with oxalic and sulfuric acids accompanying the loss of four molecules of water to give the spirolactone of dibenzo[c,h]xanthene. The reaction appears to be general for α-naphthol derivatives and p-substituted phenols.

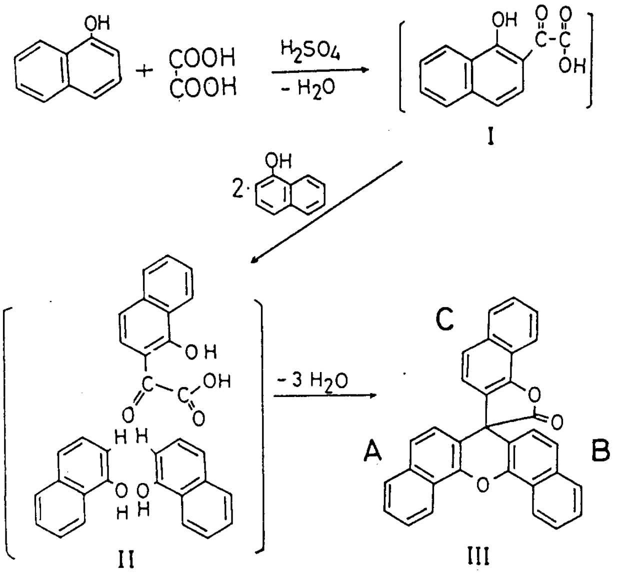
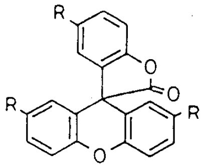


Chart 1



IV: R=Cl
V: R=Me

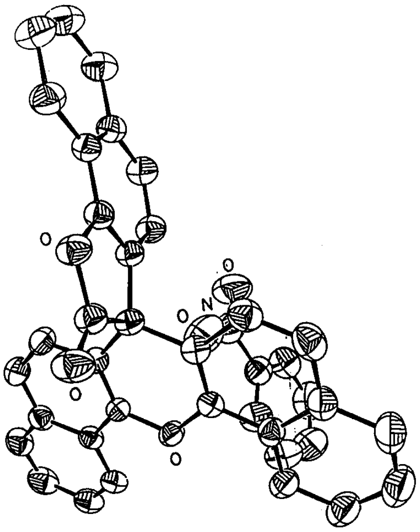


Fig. 1

The corresponding spirolactones of xanthenes (IV and V) were obtained by utilizing the p-chloro- and p-methylphenols in place of α-naphthol. The molecular structures of IV and V were also determined by X-ray diffraction methods.[6]

Further studies are in progress to increase the examples of this interesting reaction and will be reported with the X-ray data in due course.

ACKNOWLEDGEMENT The authors are grateful to Professor M. Kakudo, Dr. N. Yasuoka, Mr. K. Sakaguchi, and the staffs of Crystallographic Research Center, Institute for Protein Research, Osaka University, for the X-ray diffraction experiment and computing facilities. The authors are also grateful to Dr. A. Kato, Niigata College of Pharmacy, for the mass spectra data measurement.

REFERENCES AND NOTES

1) M. Kimura, I. Okabayashi and N. Yasuoka, Chem. Pharm. Bull., in press.
2) I. Okabayashi, J. Heterocycl. Chem., **19**, 437 (1982).
3) I. Okabayashi, J. Heterocycl. Chem., **17**, 1339 (1980).
4) The yellow crystals changed to dark brown color at 162 °C and melted completely at 312 °C.
5) G. Germain, P. Main and M. M. Woolfson, Acta Crystallogr., Sect. A, **27**, 368 (1971).
6) Compound IV: mp 239 °C; IR ν_{max}^{KBr} cm^{-1} 1630, 1790(C=O); MS m/z: 402(M^+), 374(M^+-CO), 357(M^+-CO-OH), 339(M^+-CO-OH-H_2O). The structure was determined by the X-ray diffraction method using Cu Kα radiation. Crystal data: monoclinic C2/c, a=21.316(9), b=17.267(4), c=9.158(6) Å, β=94.05°, V=3362.2 $Å^3$, 1933 |Fo| > 3σ(Fo).
Compound V: mp 165 °C; IR ν_{max}^{KBr} cm^{-1} 1480, 1800(C=O), 2800-3100; MS m/z: 342(M^+), 314(M^+-CO). The structure was determined by the X-ray diffraction method using Cu Kα radiation. Crystal data: C2/c, a=21.736(4), b=17.387(1) c=9.211(3) Å, β=95.13(2)°, V=3467.0 $Å^3$, 2397 |Fo| > 3σ(Fo).
These detailed X-ray data will be published elsewhere.

(Received July 23, 1983)