

A Novel 1,4-Cycloaddition Reaction of a Stable 2-Thianaphthalene Derivative: Formation and X-Ray Crystal Structure of 3-Benzoyl-1a,2-dimethoxycarbonyl-1-methylthio-1a,7b-dihydrocyclopropa[*a*]naphthalene

By MIKIO HORI,* TADASHI KATAOKA, HIROSHI SHIMIZU, SACHIO OHNO, and KEN'ICHI NARITA
(Gifu College of Pharmacy, 6-1, Mitahora-higashi 5-chome, Gifu 502, Japan)

and HIROZO KOYAMA

(Shionogi Research Laboratory, Shionogi Co., Ltd., Fukushima-ku, Osaka 553, Japan)

Summary Treatment of 1-benzoyl-2-methyl-2-thianaphthalene (**1a**) with dimethyl acetylenedicarboxylate leads to a novel 1,4-cycloaddition resulting in the formation of 3-benzoyl-1a,2-dimethoxycarbonyl-1-methylthio-1a,7b-dihydrocyclopropa[*a*]naphthalene (**2**) whose structure has been confirmed by X-ray crystallography.

WE recently reported¹ the first synthesis of stable 2-thianaphthalene derivatives, compounds (**1a**) and (**1b**), and also the determination of the structure of 1-benzoyl-2-methyl-2-

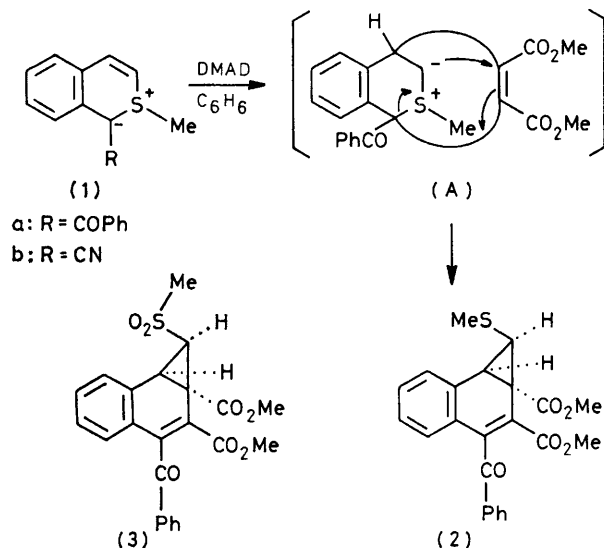
thianaphthalene (**1a**) by X-ray crystallography,² as part of a systematic investigation of thiabenzenes. We now report the reaction of (**1a**) with dimethyl acetylenedicarboxylate (DMAD).

Stirring of (**1a**) with DMAD in benzene at 60–70 °C for 4 h gave one major product, m.p. 146 °C (from EtOH), in 64% yield. Microanalytical and mass spectral data (M^+ , m/e 408) indicated a molecular formula of $C_{23}H_{20}O_5S$ corresponding to a 1:1 adduct of (**1a**) and DMAD. Its n.m.r. spectrum showed peaks at δ 2.16 (3H, s), 3.21† (1H, d,

† The high δ value may be explained by the deshielding effects of the *cis* ester group, and the value is reasonable for that of the cyclopropyl protons of benzonorcaradienes in comparison with the known related compounds (E. Ciganek, *J. Am. Chem. Soc.*, **1965**, **87**, 652; K. A. Burdett, F. L. Shenton, D. H. Yates, and J. S. Swenton, *Tetrahedron*, **1974**, **30**, 2057; D. M. Madigan and J. S. Swenton, *J. Am. Chem. Soc.*, **1970**, **92**, 7513).

J 10 Hz), 3.53 (3H, s), 3.59† (1H, d, J 10 Hz), 3.75 (3H, s), 7.00–7.80 (7H, m,) and 8.10–8.40 (2H, m), and its i.r. spectrum carbonyl absorptions at 1731 and 1735 (ester), and 1676 cm^{-1} (benzoyl).

Oxidation with *m*-chloroperbenzoic acid gave the sulphone (3), m.p. 224 °C (from dichloromethane–ether), whose



n.m.r. spectrum showed downfield methine peaks at δ 3.40 (1H, d, J 10 Hz) and 3.78 (1H, d, J 10 Hz) indicating that the two methine protons of (3) were attached to the carbon atoms directly bonded or conjugated with the sulphur atom. These data are in good accordance with the structure (2) for the cyclo-adduct, and this was confirmed by X-ray analysis.

Crystal data: $\text{C}_{23}\text{H}_{20}\text{O}_5\text{S}$ (2), orthorhombic, space group $Pna2_1$, $a = 7.979(2)$, $b = 27.458(7)$, $c = 9.330(3)$ Å, $Z = 4$. Data were collected on a Hilger and Watts automatic four-circle Y 290 diffractometer controlled by a PDP 8 computer. Integrated intensities were measured for $\theta < 27.5^\circ$ by the ω - 2θ scan technique with Mo- K_α radiation, and 1855 of these above background were used for the structure determination. The structure was solved by the program SEARCHER, for automatic heavy-atom analysis, and refined by full-matrix anisotropic least-squares calculations to R 0.080 for observed reflections. All hydrogen atoms were located from a difference Fourier synthesis. Values of the bond distances and angles were as expected.†

The probable mechanism for the formation of (2) involves the 1,4-cycloaddition of DMAD to the ylide (1a) followed by intramolecular Michael-type addition of the resulted thiochroman ylide intermediate (A) to the maleate moiety as shown in the Scheme.

This novel reaction provides a new route to benzonorcaradiene derivatives.

(Received, 16th January 1981; Com. 049.)

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

¹ M. Hori, T. Kataoka, H. Shimizu, K. Narita, S. Ohno, and H. Aoki, *Chem. Lett.*, 1978, 251.

² M. Hori, T. Kataoka, H. Shimizu, S. Ohno, K. Narita, H. Takayanagi, H. Ogura, and Y. Iidaka, *Tetrahedron Lett.*, 1979, 4315.