

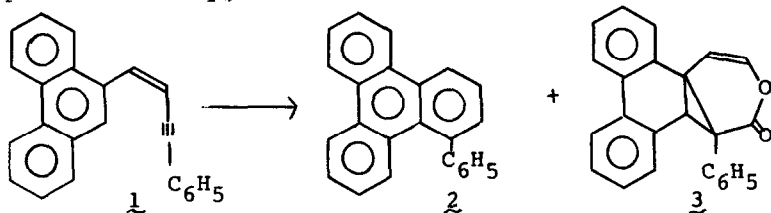
THE FORMATION OF A CYCLOPROPAPYRONE IN THE PHOTOCYCLIZATION OF
1-(9-PHENANTHRYL)-4-PHENYLBUT-1-EN-3-YNE

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Recently the photocyclization has been reported¹ of a large group of 1,4-diarylbut-1-en-3-yne into aryl-substituted aromatic compounds. It was shown that the mechanism of the reaction depends on the solvent used. In an aprotic solvent a radical mechanism, in an alcoholic solution an ionic mechanism had to be accepted. The cyclizations were found to occur from the singlet state. Extending our research on this subject a new reaction has now been found on irradiation of 1-(9-phenanthryl)-4-phenylbut-1-en-3-yne (1) in benzene in the presence of oxygen. Irradiation of 1 in benzene under nitrogen leads to the "normal" product, 1-phenyl triphenylene (2: m/e 304, mp 159-160)². Spectral data are in accordance with literature³. The same product is obtained in methanol, even in the presence of oxygen (see table).

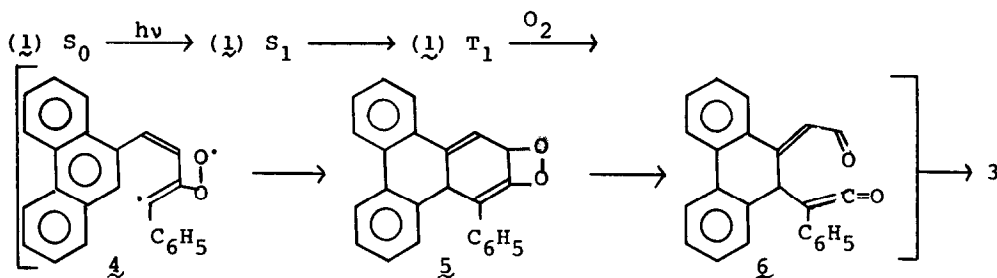


| solvent | atmosphere | yield |
|----------|----------------------------------|-----------------------------|
| methanol | N ₂ or O ₂ | 60% <u>2</u> |
| benzene | N ₂ | 58% <u>2</u> |
| benzene | air | 28% <u>2</u> , 33% <u>3</u> |
| benzene | O ₂ | 3% <u>2</u> , 61% <u>3</u> |

In apolar solvents (benzene, hexane, ether), however, irradiation without exclusion of oxygen gives 3 as the main product (m/e=336 (1: m/e=304); analysis: calculated for C₂₄H₁₆O₂: C 85.69, H 4.79, O 9.52%; found: C 85.3, H 4.9%). The structure of 3 was elucidated by spectroscopical and chemical methods. The U.V. spectrum (λ_{max} (log ϵ) methanol: 307 (3.51), 295 (3.65), 282 (4.04), 278 (4.03), 269 (4.03), 216 (4.56)) did not show the characteristics of a phenanthrene-like

spectrum. In the I.R. spectrum a strong peak at 1730 cm^{-1} but no hydroxyl absorption was present. This pointed to an unsaturated ester or lactone. Indeed, on hydrolysis of **3** one or more compounds having a carboxylic function appeared to be present in the reaction mixture. The proton nmr spectrum in CDCl_3 possessed a complex multiplet of eight protons at δ 7.72-7.10, a five proton multiplet at δ 6.98-6.46, two olefinic protons at δ 6.62 and 6.03 ($J=6.15\text{ Hz}$) and one methine singlet at δ 3.38 ppm. The high field position of five aromatic protons points to a strongly shielded phenyl moiety. In the ^{13}C nmr spectrum in CDCl_3 an ester carbon was observed at δ 168.4, two olefinic carbons at δ 139.7 ($^1J=199.6\text{ Hz}$, characteristic for enolic esters⁴) and δ 110.8 ($^1J=170\text{ Hz}$) and three saturated C atoms, two quarternary at 37,2 and 36,3 ppm and one at δ 40.5 ($^1J=168\text{ Hz}$), which points to a cyclopropane structure. The structure (**3**) derived from these data was finally confirmed by an X-ray structure determination⁵. As **3** arises only in apolar solvents a radical mechanism is probable. By irradiations of **1** with a triplet sensitizer and a triplet quencher it could be established that the reaction occurs, at least in part, from the triplet state of **1**.

Singlet oxygen nor singlet oxygen quenchers had any effect on the formation of **3**. Taking into account these facts the following pathway for the formation of **3** is suggested.



It is well known that dioxetans like **5** undergo rapidly a ring opening reaction⁶, and that phenylketenes (like **6**) react thermally with α,β -unsaturated aldehydes⁷ under formation of β - and δ -lactones. It is not surprising that in an intramolecular addition only a δ -lactone is formed. Trapping of **6** with an amine or alcohol appeared not to be possible; under these conditions only **2** was formed.

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