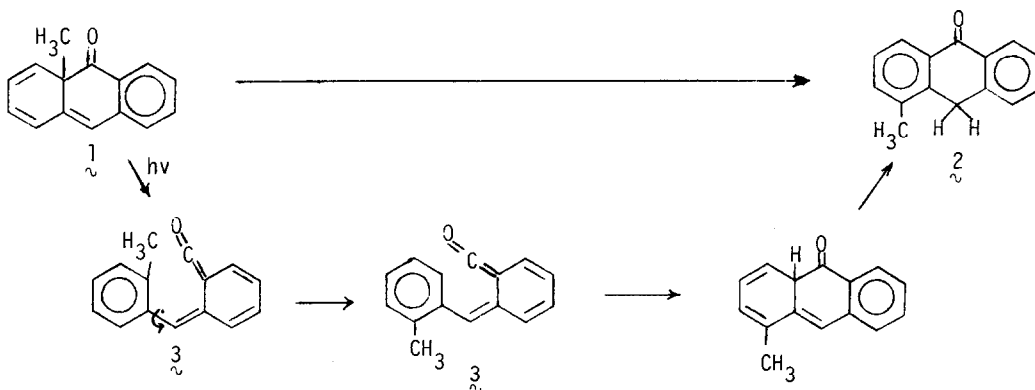


AROMATICITY-SWITCHING STEPS IN THE PHOTOREARRANGEMENT OF A
KETONE WITH FUSED BLOCKED AROMATIC RINGS

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Reactions requiring disruption of aromatic rings tend to be much slower than similar reactions of nonaromatic molecules. We now wish to report a series of facile electrocyclic reactions in which disruption of the aromaticity of one ring is accompanied by simultaneous aromatization of another ring. Such "aromaticity-switching reactions" have only rarely been observed before this.¹

Photoirradiation of ketone **1** in benzene, ether, or chloroform solution (typically by a 275 watt sun lamp at a distance of 6" for 33 minutes at 0°) yielded 4-methylanthrone (**2**)³ as the only detectable product (92-96% isolated yield). Anthrone **2** was identical with a sample prepared by Friedel-Crafts cyclization of *o*-(*o*-methylbenzyl)benzoic acid.³



Although conversion of **1** to **2** formally represents a [1,5] methyl shift, the reaction actually proceeds by the series of electrocyclic reactions shown above. The intermediacy of ketene **3** was established by trapping experiments. Although photoirradiation of **1** in methanol solution formed **2** in quantitative yield, irradiation in diethylamine solution formed amide **4** in 79% yield. The



structure of **4** was confirmed by independent synthesis from *o*-(*o*-methylbenzyl)-benzoic acid. When irradiation of **1** (in benzene solution) was carried out in the presence of four molar equivalents of maleic anhydride, adduct **5** (m.p. 219-222°) was obtained. No reaction between **1** and diethylamine or maleic anhydride could be detected in the dark at room temperature, while at higher temperatures maleic anhydride reacts with **1** to form a simple Diels-Alder adduct, rather than one derived from rearrangement of **1**.²

Formation of ketenes by photoirradiation of cyclohexa-2-dien-1-ones is a well known process.⁴ However, attempts to intercept a ketene intermediate in the photorearrangement of naphthalenone **6** were unsuccessful.⁵



Our observations indicate that ketenes are readily formed from cyclohexadienones if no disruption of an aromatic ring is necessary, or if disruption of one ring is accompanied by aromatization of a second, but apparently not if net loss of an aromatic sextet is necessary.

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