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THE PHOTOOXIDATION OF 1-METHYLANTHRAQUINONE AND o-METHYLACETOPHENONE

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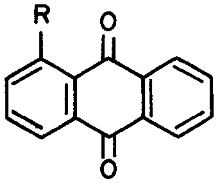
It has been found that photooxidation of a number of o-methylaryl ketones gives products in which the methyl group is converted to a carboxylic acid group or becomes the carbonyl group of a lactone ring. Such products have been obtained from anthraquinone, 1,4-naphthoquinone, xanthone, and acetophenone derivatives. We report here on the cases of 1-methylanthraquinone and o-methylacetophenone.

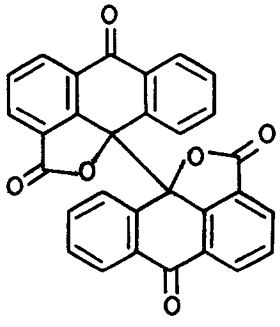
Exposure of a 0.1% solution of 1-methylanthraquinone (I) in benzene to sunlight in the presence of air for 6 days gave anthraquinone-1-carboxylic acid (II) (54%) (1) and anthraquinone (III) (8%). A third compound was shown to be present by a strong band at 5.6 μ in the infrared spectrum ($CHCl_3$) of the benzene-soluble fraction of the crude product. This compound was obtained as the major product (60%) when a 1% solution of I in benzene presaturated with oxygen was irradiated in pyrex with a 450-w. Hanovia medium-pressure mercury arc lamp and a G.E. 270-w. sunlamp. It was isolated by removal of other components of the crude reaction product with hot acetic acid; crystallization of the insoluble residue from nitrobenzene gave colorless crystals, m.p. 304-306°, λ_{max} (Nujol) 5.65, 6.00, 6.31 μ. It was assigned the molecular formula $C_{30}H_{14}O_6$ on the basis of elemental analytical and mass spectral data; the peak with highest m/e (apart from isotopic satellites), which was also the base peak, appeared at 235 and was considered to arise by fragmentation of the molecule into two fragments of equal mass (metastable peak at ~118). It was shown to be the dilactone IV by direct comparison with a sample, m.p. 304-306° [lit. (2) 282°], prepared by oxidation of the lactone V with boiling nitrobenzene (2,3).



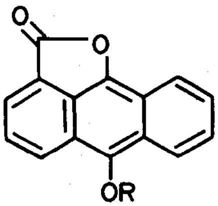
I, R = CH_3 VIII, R = CHO

II, R = CO_2H XI, R = C_2H_5

III, R = H XII, R = $COCH_3$

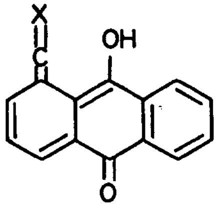


IV



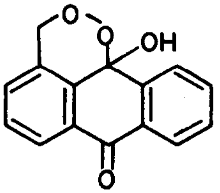
V, R = H

X, R = $COCH_3$



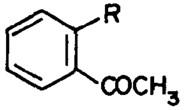
VI, X = H_2

IX, X = O



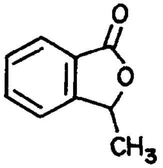
VII

Studies by Yang (4) and Ullman (5) and coworkers suggest that photooxidation of I proceeds via photoenolization to VI which is converted in turn to the peroxide VII and the aldehyde VIII. Photoenolization of VIII to the ketene IX followed by intramolecular attack of the hydroxyl group at the ketene group would give the lactone V or its ketonic tautomer (6). Facile oxidation of either tautomer to the dilactone IV finds ample precedent in the case of analogous lactones (2,7). Oxidation of VIII or IX could also account for the formation of the carboxylic acid I, while photodecarbonylation of VIII could lead to anthraquinone. The following evidence corroborating the occurrence of these processes has been obtained: (a) irradiation of I in methanol-<u>d</u>/benzene in the absence of oxygen led to the incorporation of deuterium into the methyl group (8) (b) irradiation of I in acetic anhydride in the presence of air gave, <u>inter al.</u>, the aldehyde VIII (9) and the lactone X (c) irradiation of VIII in benzene in the presence of air gave the dilactone IV (d) photooxidation of 1-ethylanthraquinone (XI) gave 1-acetylanthraquinone (XII) (e) photooxidation of 2-methylanthraquinone and 2-ethylanthraquinone to give anthraquinone-2-carboxylic acid and 2-acetylanthraquinone, respectively, occurred very much more slowly than did the photooxidation of I and XI.

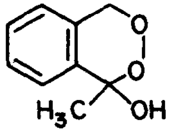


XIII, R = CH_3

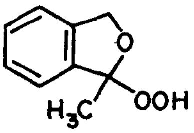
XVII, R = CHO



XIV



XV



XVI

Irradiation of *o*-methylacetophenone (XIII) in acetic anhydride in the presence of air gave 3-methylphthalide (XIV). In this case it was found possible to isolate the intermediate peroxide XV, the analog of the postulated intermediate VII, by irradiation of XIII in benzene in the presence of oxygen; further irradiation of XV in either benzene or acetic anhydride gave XIV. The structure of XV is assigned on the basis of spectroscopic data [δ ($CHCl_3$) 1.65 (s, 3H), 4.0 (broad, conc. dependent, 1H), 4.83 and 5.36 (AB, J = 15.5 Hz, 2H), 7.33 (m)] and of the demonstration that the compound is not the hydroperoxide XVI, m.p. 88-89.5°, which was prepared by an independent route. The intermediacy of the aldehyde, XVII, analogous to VIII, is suggested by the observation that this aldehyde, obtained by treatment of XV under acidic conditions, is converted to XIV on irradiation in benzene in the presence of air. The isolation of XIV in this case, rather than a bimolecular product analogous to IV, must reflect the greater susceptibility to oxidation of the monolactone in the anthraquinone series.

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REFERENCES

1. Cf. A. Eckert, *Ber.* **58**, 313 (1925).
2. R. Scholl and H.-D. Wallenstein, *Ber.* **69**, 503 (1936); R. Scholl and F. Renner, *Ber.* **62**, 1278 (1929).
3. The possibility that the photochemical product was lactone V, which was oxidized to IV during the crystallization of the crude product from nitrobenzene, was excluded by comparison of the properties of the product prior to crystallization with those of IV and V.
4. N. C. Yang and C. Rivas, *J. Am. Chem. Soc.* **83**, 2213 (1961).
5. K. R. Huffman, M. Loy, and E. F. Ullman, *J. Am. Chem. Soc.* **87**, 5417 (1965); W. A. Henderson, Jr., and E. F. Ullman, *J. Am. Chem. Soc.* **87**, 5424 (1965).
6. Evidence for the occurrence of such a process in the case of the photoreaction of *o*-phthalaldehyde has very recently been reported by S. P. Pappas and J. E. Blackwell, Jr., *Tetrahedron Letters*, 3337 (1968).
7. Cf. H. H. Wasserman, T.-C. Liu, and E. R. Wasserman, *J. Am. Chem. Soc.* **75**, 2056 (1953); P. Yates and T. J. Clark, *Tetrahedron Letters*, 435 (1961).
8. Cf. Reference 4; we thank Professor N. C. Yang, University of Chicago, for providing us with further details of his deuterium-exchange experiments.
9. Identified by comparison with a sample prepared by treatment of 1-(bromomethyl)anthraquinone with dimethyl sulfoxide and collidine.