the crude lithium or sodium sulfinate washed with water, acetone and ether. It was then identified by conversion to its 2,4-dinitrophenyl sulfone[31b] or to the disulfone with dibromoethane.[32]

Attempted cleavage of *p*-carbethoxyphenyl phenyl sulfide was carried out as described above with two equivalents of lithium. The only identifiable product on workup was *p*-phenylmercapto-N-methylbenzamide, m.p. 101–102° after two recrystallizations from ethanol–water. Basic hydrolysis followed by acidification yielded *p*-phenylmercaptobenzoic acid, m.p. 173° (literature[33] 173° uncor.). This acid produced no depression of melting point in a mixture melting point determination with an authentic sample obtained by the basic hydrolysis of the original ester. Infrared showed the presence of characteristic amide absorption and the odor of methylamine was quite noticeable during the amide hydrolysis.

Acknowledgment.—The authors wish to express their gratitude for the financial support of this study by the Standard Oil Company of Ohio, and by the National Cancer Institute, National Institutes of Health, Grant CY-4536.

LAFAYETTE, IND.

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(32) P. Allen, *J. Org. Chem.*, **7**, 23 (1942).

(33) W. S. Weedon and H. W. Doughty, *Am. Chem. J.*, **33**, 425 (1905).

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORY OF THE SOCONY MOBIL OIL CO., INC., AND THE WHITMORE LABORATORY OF THE COLLEGE OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE UNIVERSITY]

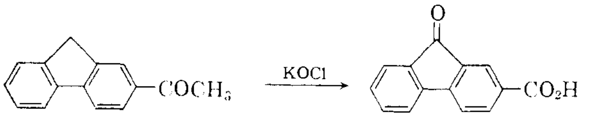
The Oxidation of Methylene and Methyl Groups by Sodium Hypochlorite[1]

BY DAVID D. NEISWENDER, JR.,[2] WILLIAM B. MONIZ AND JOSEPH A. DIXON

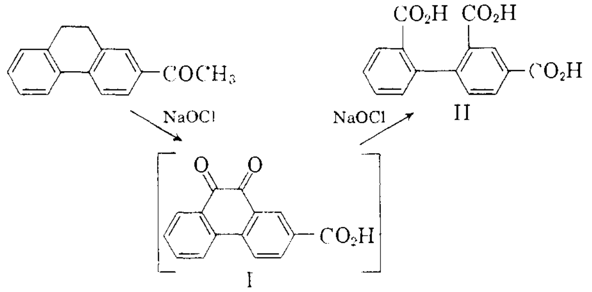
RECEIVED OCTOBER 15, 1959

Methylene and methyl groups attached to an aromatic nucleus are readily oxidized by sodium hypochlorite when the nucleus also contains an acetyl group. The acetyl group seems to play a vital role in the oxidations, and a mechanism has been suggested to explain this. Sodium hypochlorite has been found to oxidize aromatic α-diketones such as benzil and 9,10-phenanthrenequinone.

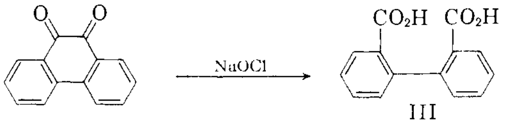
The oxidation of methyl ketones to carboxylic acids by means of alkaline hypohalite solutions is a well known and widely used technique. The reaction has been extended to higher alkylaryl ketones and alkylheterocyclic ketones.[3,4] Recently, Farrar has reported on the hypobromite oxidation of cyclic ketones to dicarboxylic acids.[5] The first report of the attack of hypohalite on a methylene group was that of Schiessler and Eldred.[6] They attempted to prepare fluorene-2-carboxylic acid by oxidizing 2-acetylfluorene, but instead obtained only fluorenone-2-carboxylic acid.



The present research was initiated when a similar anomalous oxidation was discovered. In attempting to prepare 9,10-dihydrophenanthrene-2-carboxylic acid from 2-acetyl-9,10-dihydrophenanthrene by oxidation with sodium hypochlorite (*p*H 12–13), an unexpected product was obtained. Analysis of the substance showed it to be 2,2′,4-tricarboxybiphenyl (II). The hypochlorite had oxidatively cleaved the 9,10-bond in the dihydrophenanthrene nucleus. When sodium hypochlorite solution with a *p*H of approximately 10 was used, the major oxidation product was the normal one, 9,10-dihydrophenanthrene-2-carboxylic acid. A small amount of the triacid was also produced.



It is interesting to note that the starting ketone differs from 2-acetylfluorene by only one methylene group. Considering the ketone obtained by Schiessler and Eldred, one might reasonably expect the quinone I to be an intermediate in the oxidation process. To test this hypothesis, 9,10-phenanthrenequinone was treated with sodium hypochlorite and converted in a 94% yield to diphenic acid (III). Benzil was oxidized to benzoic acid in 88% yield. These two experiments lend support to the suggestion that the phenanthrenequinone is an intermediate.



When 6-acetyltetralin was oxidized, an 18% yield of the normal product, tetralin-6-carboxylic acid, was obtained along with a 56% yield of a mixture of tricarboxylic acids. Upon separation, the acid obtained in lesser quantity was identified as 3-(2,4-dicarboxyphenyl)-propanoic acid (IV), while the predominant acid is believed to be the isomeric 3-(2,5-dicarboxyphenyl)-propanoic acid (V). The latter has not been reported previously.

p-Ethylacetophenone was converted to terephthalic acid in 95% yield. In order to determine

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(1) Presented in part before the Division of Organic Chemistry at the 135th Meeting of the American Chemical Society, Boston, Mass., April, 1959.

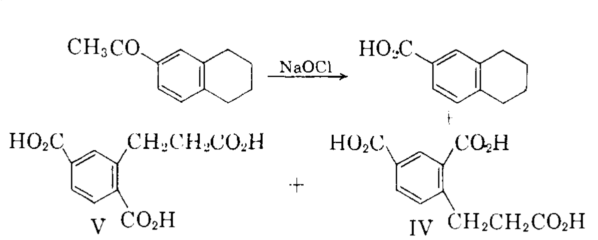
(2) Research and Development Laboratory, Socony Mobil Oil Co., Inc., Paulsboro, N. J. To whom inquiries may be sent.

(3) M. W. Farrar and R. Levine, THIS JOURNAL, **71**, 1496 (1949).

(4) R. Levine and J. A. Stephens, *ibid.*, **72**, 1642 (1950).

(5) M. W. Farrar, *J. Org. Chem.*, **22**, 1708 (1957).

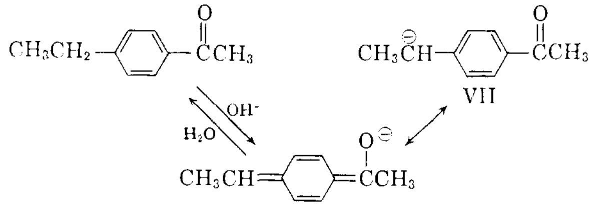
(6) R. W. Schiessler and N. R. Eldred, THIS JOURNAL, **70**, 3958 (1948).



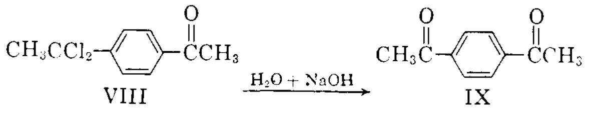
whether methyl groups can be similarly oxidized, *p*-methylacetophenone was treated with sodium hypochlorite to produce 47% of terephthalic acid. Apparently, a methylene group adjacent to an aromatic ring is more readily attacked than a similarly placed methyl group.

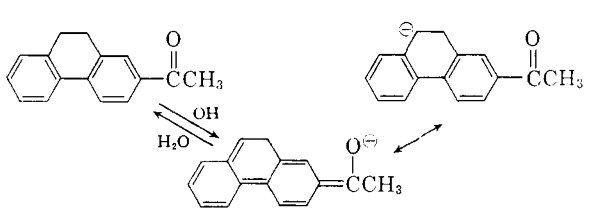
Investigations have shown that the acetyl group plays a very important role in the oxidation. Schiessler and Eldred[6] were unable to oxidize fluorene to fluorenone under the conditions used to oxidize acetylfluorene. The present work has revealed that ethylbenzene is unreactive under the exact conditions used to oxidize *p*-ethylacetophenone. It was originally thought that the acetyl group aided the reaction merely by solubilizing the organic compound in the aqueous hypochlorite solution. However, it is now suspected that the acetyl group is also intimately involved in the mechanism of these oxidations.

It has been demonstrated[7,8] that the initial and rate-determining step of the haloform reaction is the enolization of the ketone. It is believed that a similar step occurs in the oxidations reported herein. Using *p*-ethylacetophenone as an example, the suggested mechanism is

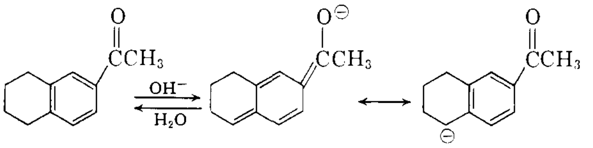


The resonance between VI and VII suggests the hybrid is a fairly stable intermediate. Chlorination of VII to the monochloro compound would then make further enolization even more favorable. The second chlorination would produce VIII, which could readily hydrolyze to the diketone IX. Of course, from this point on, the normal haloform reaction could occur, ultimately ending in the production of terephthalic acid. An enolate type intermediate can also be written for the acetyldihydrophenanthrene (see next formula diagram). In this particular example, experiments have shown that high *p*H (12–13) favors the formation of the tricarboxylic acid II while lower *p*H (*ca.*10) favors production of the dihydrophenanthrenecarboxylic acid. These results support the proposed enolization mechanism. Successive chlorination of the enolate ions, followed by hydrolysis of the dichloride could produce a ketone and subsequently a quinone. The mechanism of the oxidative cleavage of the quinone intermediate is not known at present.





In the case of 6-acetyltetralin, where two products other than the normal one were obtained, the explanation may be as follows: Both α-methylene groups, since they are benzilic in nature, might be attacked to some extent. However, only the methylene group *para* to the acetyl group can be involved in the enolate ion resonance



Supporting this theory is the fact that the predominant isomer obtained in the oxidation is the one expected from the enolate ion as drawn.

All the enolizations postulated seem logical, since in each case the aromatic ring system is involved in the resonance hybrid and thus should impart stability to the enolate ion.

Since the inductive effect of the acetyl group might conceivably contribute to the oxidation of the alkyl side chains, a further experiment was performed. The methyl group in *m*-methylacetophenone cannot be activated by enolate ion resonance: therefore, it was treated with hypochlorite in the same manner as was *p*-methylacetophenone. A 13% yield of isophthalic acid was obtained, the major product being *m*-toluic acid. This compares with a 47% yield of terephthalic acid from *p*-methylacetophenone. Thus the inductive effect does contribute, but not to as great an extent as does the enolate ion resonance. Further research on the mechanism of these oxidations is planned.

Experimental[9]

Oxidation of 2-Acetyl-9,10-dihydrophenanthrene. 1.—2-Acetyl-9,10-dihydrophenanthrene (4.0 g.), prepared by the method of Riegel,[10] was stirred under nitrogen at 60–80° for 19 hours with 800 ml. of sodium hypochlorite solution containing an additional 2.0 g. of sodium hydroxide. After destroying the excess hypochlorite with sodium bisulfite, the solution was extracted with ether to remove any unreacted ketone. Only a trace of non-volatile material was obtained from the ether extract. The aqueous solution, on acidification, yielded 2.5 g. (49% yield) of a white solid, insoluble in benzene and melting at 247–262°. The expected compound, 9,10-dihydrophenanthrene-2-carboxylic acid, is soluble in benzene and melts at 211–212°.[11] Two recrystallizations from 50% acetic acid produced white crystals melting at 265–267°. The elemental analysis and

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[7] P. D. Bartlett, THIS JOURNAL, **56**, 967 (1934).

[8] R. P. Bell and H. C. Longuet-Higgins, *J. Chem. Soc.*, 636 (1946).

[9] Melting points are uncorrected. The sodium hypchlorite solution, unless otherwise noted, was a commercially available 5% solution with a *p*H of 12–13.

[10] B. Riegel, *et al.*, THIS JOURNAL, **64**, 2221 (1942).

[11] A. Burger and E. Mosettig, *ibid.*, **57**, 2731 (1935).

neutral equivalent of the substance indicate it to be 2,2′,4-tricarboxybiphenyl (II), a previously unreported compound.

Anal. Calcd. for $C_{15}H_{10}O_6$: C, 62.9; H, 3.5; neut. equiv., 95.4. Found: C, 62.4; H, 3.8; neut. equiv., 94.3.

2.—Different results were obtained when a sodium hypochlorite solution with a *p*H of about 10 (the *p*H of a 5% solution of the salt) was employed. The ketone (3.0 g.) and 400 ml. of the hypochlorite solution were refluxed under nitrogen for 9 hours. On cooling, a sodium salt precipitated which, on acidification, yielded 1.0 g. of 9,10-dihydrophenanthrene-2-carboxylic acid, m.p. 215.0–216.5°. Acidification of the aqueous solution yielded a mixture of acids weighing 1.0 g. Recrystallization from 50% acetic acid yielded another 0.3 g. of 9,10-dihydrophenanthrene-2-carboxylic acid, m.p. 215.0–216.5°, and 0.3 g. of the tricarboxybiphenyl, m.p. 262–268°.

Oxidation of 9,10-Phenanthrenequinone.—The quinone (4.0 g.) and 500 ml. of sodium hypochlorite solution were refluxed under nitrogen for 22 hours. The hot solution was treated with sodium bisulfite and acidified. Chilling the solution caused 1.70 g. of lustrous white crystals to precipitate. The aqueous solution was saturated with salt and extracted with ether. The extracts contained 2.61 g. of the product. The total, 4.31 g., constituted a 94% yield of crude diphenic acid, m.p. 219–222°. After recrystallization from water, the acid melted sharply at 220–221°.

Anal. Calcd. for $C_{14}H_{10}O_4$: C, 69.42; H, 4.16. Found: C, 69.12; H, 4.13.

Oxidation of Benzil.—A mixture of benzil (5.0 g.) and 300 ml. of sodium hypochlorite solution were gently refluxed under nitrogen for 20 hours. The excess hypochlorite was destroyed and the solution acidified. There resulted 5.1 g. (88% yield) of benzoic acid (m.p. 121–122°, mixed m.p. 121–122°).

Oxidation of 6-Acetyltetralin.—6-Acetyltetralin (22.0 g.) and 0.58 *N* sodium hypochlorite (prepared by bubbling chlorine into 3 liters of water containing 260 g. of sodium hydroxide) were stirred under nitrogen at 86° for 14 hours. Acidification of the reaction mixture precipitated 3.9 g. of white crystals which were dissolved in benzene and percolated over silica gel using acetone as the eluent. The solid was then recrystallized from ethanol–water and shown to be the normal oxidation product, 6-tetralincarboxylic acid; calcd. neut. equiv. for $C_{11}H_{12}O_2$ 176, found 170; m.p. 153–156°, reported 154–155°.

Ether extraction of the acidified reaction mixture yielded 16.8 g. of a tan solid. Chromatographic treatment of the solid over silica gel using chloroform–acetone and then acetone as the eluents showed that two products other than the tetralincarboxylic acid were formed. They are 3-(2,4-dicarboxyphenyl)-propanoic acid (IV) and an isomer believed to be 3-(2,5-dicarboxyphenyl)-propanoic acid (V). The latter is the predominant product.

Anal. Calcd. or reported for $C_{11}H_{10}O_6$: C, 55.5; H, 4.2; neut. equiv., 79.4; m.p. 265–266° (for the 2,4-isomer; m.p. of 2,5-isomer is unknown). Predominant isomer: Found: C, 55.3; H, 4.4; m.p. 230–232°; neut. equiv., 80.1. Other isomer: Found: C, 55.2; H, 4.5; m.p. 251–257°.

Oxidation of *p*-Ethylacetophenone.—*p*-Ethylacetophenone (5.0 g.) and 800 ml. of sodium hypochlorite solution were refluxed gently under nitrogen for 44 hours. After destruction of the excess hypochlorite, acidification of the solution produced 5.24 g. (95% yield) of terephthalic acid.

Anal. Calcd. for $C_8H_6O_4$: C, 57.8; H, 3.64; neut. equiv., 83.1. Found: C, 57.5; H, 3.69; neut. equiv., 84.5.

The acid was identified further through its dichloride, prepared from the acid and phosphorus pentachloride; m.p. 77.5–79° reported m.p. 79–80°.

Oxidation of *m*- and *p*-Methylacetophenone.—The methylacetophenone (5.0 g.) and 800 ml. of sodium hypochlorite solution were treated exactly as described in the above experiment. The oxidation of the *m*-methylacetophenone yielded 0.8 g. (13% yield) of isophthalic acid while the *p*-isomer yielded 2.9 g. (47% yield) of terephthalic acid. The acids were identified by means of their dichlorides.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF NORTHWESTERN UNIVERSITY]

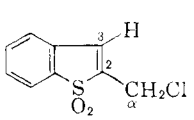
SN2 and SN2′ Reactions of 2- and 3-Chloromethylbenzothiophene 1,1-Dioxides

BY F. G. BORDWELL, FRANK ROSS AND JOSEPH WEINSTOCK

RECEIVED MAY 20, 1959

The reactions of piperidine, thiourea and sodium thiophenoxide with 2-chloromethylbenzothiophene 1,1-dioxide (I) were found to be normal SN2 displacements, but 3-chloromethylbenzothiophene 1,1-dioxide (II) was attacked by these reagents, and also by morpholine at the $C_2{=}C_3$ bond. The latter are the only known examples in which a primary allylic halide has been found to react with nucleophilic reagents by an SN2′ mechanism.

This study was initiated several years ago[1] on the basis that substitution of the strongly electron-attracting sulfonyl group[2] into the β- or γ-position of an allylic system, $\overset{\gamma}{C}{=}\overset{\beta}{C}{-}\overset{\alpha}{C}{-}X$, would probably reduce the electron density of the C=C bond, and thereby favor reaction of nucleophilic reagents at the γ-position resulting in reactions by SN2′ mechanisms. The 2- and 3-chloromethylbenzothiophene 1,1-dioxides (I and II) appeared to be compounds of the desired type. Earlier studies have shown that the $C_2{=}C_3$ bond in benzothiophene 1,1-dioxide is aliphatic in nature.[3] The allylic systems present in I and II are unique in that activation by the sulfonyl group in each can operate from a β- and/or a γ-position. Thus in I the sulfonyl group is attached to the β-carbon, but it can also exert its influence from the γ-position by operating through the benzene ring; the situation is just reversed for II.



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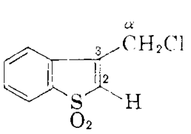

II

The desired chloromethyl sulfones I and II were readily prepared by the peracetic acid oxidation of the previously known 2-chloromethyl-[4] and 3-

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[1] An account of the work described in this paper was given at the 124th Meeting of the American Chemical Society, Chicago, Ill., September, 1953; see Abstracts, p. 60-O.

[2] F. G. Bordwell and G. D. Cooper, THIS JOURNAL, **73**, 5187 1951).

[3] F. G. Bordwell and W. H. McKellin, *ibid.*, **72**, 1985 (1950).

[4] F. F. Blicke and D. G. Sheets, *ibid.*, **71**, 2856 (1949).