

Carbonyl and Thiocarbonyl Compounds. Part XIII.¹ 2-Aroyl-1,3-benzodioxoles of Potential Pesticidal Activity and their Cleavage with Hydrazines

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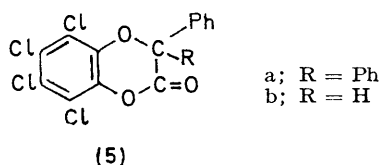
2-Aroyl-4,5,6,7-tetrahalogeno-1,3-benzodioxoles (1) are readily obtained through the uncatalysed interaction between tetrahalogeno-*o*-benzoquinones and the corresponding α -diazo-acetophenone or -acetophenone. They behave differently from all other methylenedioxy-compounds previously investigated with respect to cleavage by nucleophilic reagents. They react with phenylhydrazine in boiling *n*-butanol affording the corresponding arylglyoxal bisphenylhydrazones (6) in high yields. However, they resist cleavage by benzoylhydrazine, by malononitrile, and by cyanoacetic ester under similar conditions. The reaction mechanism is discussed. The osazones obtained are cyclised readily by copper sulphate in aqueous dioxan, affording the corresponding 4-aryl-2-phenyl-1,2,3-triazoles (7).

COMPOUNDS containing the methylenedioxyphenyl system structure show insecticidal or synergistic (with pyrethrin and carbamates) activity.² During studies on the synthesis of new 1,3-dioxoles for pesticide research, we have investigated the action of diazo-ketones on tetrahalogeno-*o*-benzoquinones.

The hitherto unknown 2-aroyl-4,5,6,7-tetrahalogeno-1,3-benzodioxoles (1a—j) are readily obtained through the uncatalysed interaction between the corresponding

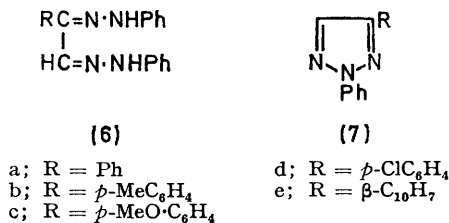
o-Quinones generally afford either 1,3-dioxoles like (1) or oxirans of type (4) on treatment with diazomethanes.³ The dioxole structure assigned to our products is inferred from their analytical data, from the fact that they are colourless whereas the reactants are highly coloured, and from their resistance to cleavage by dilute mineral acids, in contrast to the readily hydrolysable oxirans.⁴ Furthermore, the products condense readily with benzoylhydrazine in boiling *n*-butanol affording the corresponding bisphenylhydrazones (6).

tetrachloro-*o*-benzoquinone in boiling toluene. However, we find that the latter product is actually the 1,3-dioxole (1a). The suggested 1,4-dioxan (5b) would be



expected to show lactone i.r. absorption, at higher frequency than that exhibited, and its u.v. spectrum would not exhibit the absorption due to the aryl residue. The analogue (5a), as expected, exhibits ν_{CO} at 1800 cm^{-1} , and its u.v. spectrum does not show the characteristic aryl absorption.

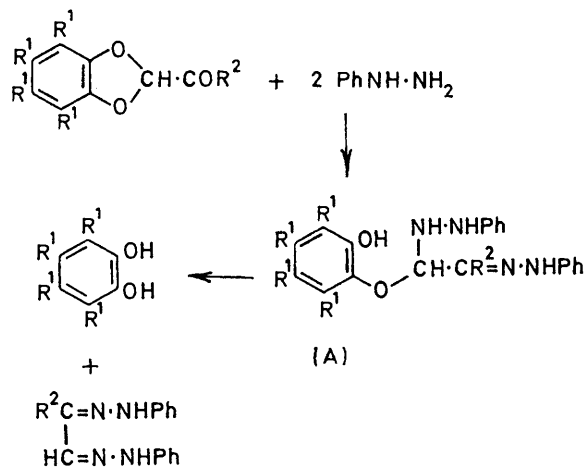
Reaction of the 1,3-Benzodioxoles (1) with Phenylhydrazine.—In contrast to the action of benzoylhydrazine on the aroylbendodioxoles (1) which simply affords the corresponding benzoylhydrazones (3), phenylhydrazine readily cleaves the dioxole ring under mild conditions (boiling *n*-butanol), affording the corresponding arylglyoxal bisphenylhydrazones (6) together with tetrachlorocatechol. The osazones (6) have been previously prepared by the action of phenylhydrazine on the corresponding diazo-ketones or the arylglyoxals themselves. The low yields obtained by the first method and the difficult accessibility of the arylglyoxals render cleavage of the aroylbendodioxoles a useful method for the preparation of the pure osazones.



Apparently cleavage of the dioxole ring proceeds through nucleophilic attack of the hydrazine on the methylene carbon atom with formation of the intermediate (A), which affords the osazone and the tetrahalogenocatechol through a β -elimination process (see Scheme). Cleavage of the dioxole ring to form intermediate (A) resembles the known nucleophilic displacement, except that the leaving group, which is the oxygen atom of the dioxole ring, remains a part of the molecule. Attempts to affect cleavage by other nucleophiles such as malononitrile and cyanoacetic ester, however, were not successful.

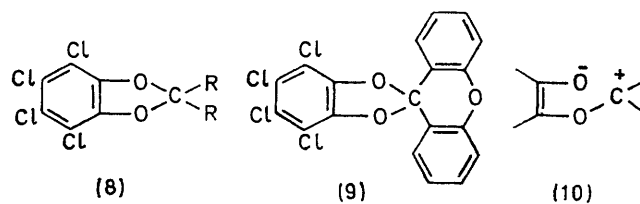
Methylenedioxy-compounds are ordinarily not reactive enough to be cleaved readily. However, we have shown that susceptibility to cleavage of the dioxole ring by nucleophilic reagents is mainly dependent on the

nature of substituents on the methylene carbon atom. Thus⁹ the methoxy-derivative (8c), in contrast to the



SCHEME

parent substances (8a and b), is readily cleaved by phenyl- and benzoyl-hydrazines, cyanoacetic ester, and malononitrile, affording the corresponding 4,4'-dimethoxybenzophenone hydrazones and 4,4'-dimethoxydiphenylmethylenemalononitrile and -cyanoacetic ester. The xanthen analogue (9) behaves similarly, affording the corresponding xanthyldene derivatives.¹⁰ This unusual ease of cleavage has been rationalised by assuming that a heteropolar structure such as (10) contributes largely to the state of the molecule.^{9,11}



a; R = H
b; R = Ph
c; R = *p*-MeO·C₆H₄

Thus 2-aryloxy derivatives differ from other 1,3-dioxoles with respect to cleavage by nucleophilic reagents. They usually behave like the parent substances (8a and b), resisting cleavage by malononitrile, cyanoacetic ester, and benzoylhydrazine. However, they resemble compounds (8c) and (9) in being readily cleaved by phenylhydrazine. These facts may be rationalised by considering that, in contrast to compounds (8c) and (9), a dipolar structure such as (10) does not contribute significantly to the state of the aroylbendodioxole molecule. However the adjacent carbonyl group and oxygen atoms confer on the methylene carbon atom sufficient electro-

⁹ N. Latif, I. Zeid, and B. Haggag, *J. Heterocyclic Chem.*, 1968, **5**, 833.

¹⁰ N. Latif, I. Fathy, and N. Mishriky, *J. Org. Chem.*, 1962, **24**, 1883.

¹¹ N. Latif and N. Mishriky, *Canad. J. Chem.*, 1966, **44**, 1291.

philic character to render it susceptible to attack by phenylhydrazine but not by the weaker nucleophiles.

Cyclisation of Arylglyoxal Osazones.—The osazones (6), obtained through cleavage of the dioxoles by phenylhydrazine, cyclise readily to give the corresponding *v*-triazoles (7). The triazole (7a) has been previously prepared.¹² The u.v. spectra of the products show the characteristic strong absorption in the 290 nm region.

U.v. spectra of compounds (1) and (7)

| Compound | $\lambda_{\max.}/\text{nm}$ | ϵ | $\lambda_{\min.}/\text{nm}$ | ϵ |
|----------|-----------------------------|------------|-----------------------------|------------|
| (1a) | 215 | 44,900 | 275 | 962 |
| (1b) | 215 | 48,100 | 270 | 952 |
| (1d) | 215 | 57,040 | 275 | 838 |
| (1g) | 220 | 49,100 | 270 | 2590 |
| (1i) | 220 | 51,980 | 285 | 2270 |
| (7a) | 293 | 25,200 | | |
| (7b) | 296 | 25,849 | | |

EXPERIMENTAL

Microanalyses were performed by the Microanalytical Laboratory, National Research Centre, Cairo, Egypt. I.r. spectra were recorded with a UR10 Zeiss Jena spectrophotometer for potassium bromide discs, and u.v. spectra with Zeiss type PMQII and Unicam SP 500 spectrophotometers.

then poured on ice. The precipitated solid was filtered off and crystallised from acetone to give unchanged benzodioxole (1) (m.p. and mixed m.p.).

Reaction of the Benzodioxoles (1) with Benzoylhydrazine.—A mixture of the benzodioxole (1) (0.01 mol) and benzoylhydrazine (0.03 mol) in *n*-butanol (15 ml) was heated under reflux for 6 h and left to cool. The separated solid was filtered off and crystallised from benzene to give the benzoylhydrazones (3).

Hydrolysis of the Benzoylhydrazone (3a).—A suspension of the benzoylhydrazone (3a) (1 g) in a solution of concentrated hydrochloric acid (4 ml) in dioxan (10 ml) was heated under reflux for 3 h. The mixture was left to cool and poured on ice. The separated solid was filtered off and crystallised from acetone to give the benzodioxole (1a) (m.p. and mixed m.p.).

Reaction of the Benzodioxoles (1) with Phenylhydrazine.—A mixture of the aryldioxole (1) (0.01 mol) and phenylhydrazine (0.03 mol) in absolute ethanol (25 ml) was heated under reflux for 1 h. The solution was concentrated and left to cool. The separated solid was filtered off and recrystallised to give the arylglyoxal bisphenylhydrazone (6).

The mother liquor from the original reaction mixture was poured into ice-cold water and acidified with dilute hydrochloric acid. The solid obtained was filtered off, washed