Attempted addition of hydrogen peroxide to bicycloheptadiene. When bicycloheptadiene was allowed to react for 24 hr. at room temperature with hydrogen peroxide (50%) in a two-phase system with stirring using chloroform or carbon tetrachloride as solvents and catalytic amounts of sulfuric acid, no organic peroxides were formed. Even in the absence of inert solvents with traces of the acid present no reaction was observed after 24 hr. of stirring. However, when the concentration of the acid was increased to about 50% and the reaction carried out at 0° with stirring but without the use of inert solvents, the mixture exploded at the end of 2 hr.; even when carbon tetrachloride was used under these conditions, the reaction produced black tars and no organic peroxides.

The following experiment led to the isolation in very small yields of a mixture of two peroxides. To a mixture of 10 g. of hydrogen peroxide (50%) and 5 g. of concd. sulfuric acid maintained at 0° was added dropwise with stirring 11 g. of bicycloheptadiene. Stirring was continued at 0° for 2.5 days, then to the mixture was added 25 ml. of saturated ammonium sulfate solution and the resulting mixture extracted several times with cyclohexane. The cyclohexane extracts were shaken again with saturated ammonium sulfate to remove traces of hydrogen peroxide, dried over magnesium sulfate, then the solvent and unused bicycloheptadiene removed under reduced pressure. A small amount of oil remained which failed to crystallize. A paper chromatogram using dimethylformamide-decalin as the developing solvent and hydriodic acid–glacial acetic acid as the detecting agent showed two strong spots; one with R_f, 0.08, and the other with an R_f, 0.76. The spot with the lower but not the one with the higher R_f was also observed when the paper chromatogram was sprayed with potassium iodide–glacial acetic acid detecting agent. This indicates that the peroxide with the lower R_f must be a hydroperoxide while the one with the higher R_f, a dialkyl peroxide. This was also confirmed by the infrared spectrum of the mixture which showed bands at 3400 and 880 cm.$^{-1}$, respectively. The amount available of the mixture was too small for separation and further investigation of these two peroxides.

Acknowledgment. The authors are indebted to Dr. I. Belič for the paper chromatographic analyses, to Dr. Nagy for the combustion analyses, to Mrs. Alvord for the infrared spectra, and to Research Corporation and Lucidol Division of Wallace and Tiernan, Inc., for the financial support of this investigation.

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Action of Acid on *o*-Aroyldiarylcarbinols. A New Route to Isobenzofurans[1]

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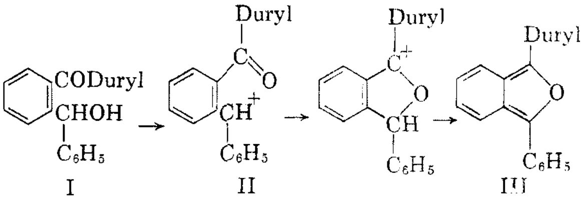
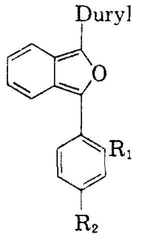
o-Duroylphenylphenylcarbinol (I) prepared by condensation of *o*-duroylphenyllithium[3] with benzaldehyde, undergoes conversion to 1-duryl-3-phenylisobenzofuran (III) when treated with strong mineral acid. The cyclodehydration presumably proceeds by way of the *o*-duroyldiphenylcarbonium ion (II).



The yield of the isobenzofuran from the carbinol was 83%, but the overall yield from the lithium reagent was only 19%. A higher overall yield may be achieved by omitting the isolation of the carbinol and using strong acid in the workup of the original reaction mixture. From the lithium compound the isobenzofuran was made by this method in a yield of 43%. This latter procedure served also to prepare 1-duryl-3-(2-methoxyphenyl)isobenzofuran (IVa), 1-duryl-3-(4-methoxyphenyl)isobenzofuran (IVb), 1-duryl-3-(2-chlorophenyl)isobenzofuran (IVc), and 1-duryl-3-(4-chlorophenyl)isobenzofuran (IVd).



IVa. $R_1 = OCH_3$, $R_2 = H$
IVb. $R_1 = H$, $R_2 = OCH_3$
IVc. $R_1 = Cl$, $R_2 = H$
IVd. $R_1 = H$, $R_2 = Cl$

The intervention of *o*-aroyldiarylcarbonium ions in the formation of isobenzofurans has not been suggested previously, but would seem to account for several of the most important syntheses of these heterocycles.[4] Thus, the formation of isobenzofurans by reductive cyclodehydration of *o*-diaroylbenzene derivatives, by treatment of α-arylphthalides with aromatic Grignard reagents, and by condensation of *o*-cyanobenzaldehyde with aromatic Grignard reagents, can be explained on this basis.

EXPERIMENTAL[5]

1-Duryl-3-phenylisobenzofuran. An ether solution of *o*-duroylphenyllithium, blanketed with dry nitrogen and maintained at −30° to −35°, was prepared by the method previously described[3] from 6.3 g. (0.02 mole) of *o*-duroylbromobenzene and 10.7 ml. of 1.86*N* *n*-butyllithium solution. To the cooled solution of the lithium reagent was added all at once, with stirring, a solution of 2.14 g. (0.02 mole) of benzaldehyde in 25 ml. of anhydrous ether. The reaction mixture was stirred at bath temperature for 15 min.; then the bath was removed, and stirring was continued for an additional 15 min. The contents of the flask

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[2] Union Carbide Fellow, 1958–1959.

[3] R. C. Fuson, W. C. Hammann, and W. E. Smith, *J. Org. Chem.*, **19**, 674 (1954).

[4] See R. Adams and M. H. Gold, *J. Am. Chem. Soc.*, **62**, 2038 (1940).

[5] All melting points are corrected.

were poured into a mixture of ice and 20% hydrochloric acid. After the ice had melted, the fluorescent organic layer was washed with 10% sodium bicarbonate solution, then with water, and dried over magnesium sulfate. The ether was distilled, and the residue was recrystallized twice from absolute ethanol to give intensely yellow crystals, m.p. 118–119°. The yield was 2.94 g. (43%). The infrared spectrum[6] of this material shows no bands for carbonyl or hydroxyl groups. The only significant band, besides those usually ascribed to a methyl group or a substituted benzene ring, appears at 1150 cm.$^{-1}$, and may be assigned to an ether linkage.[7]

Anal.[8] Calcd. for $C_{24}H_{22}O$: C, 88.31; H, 6.79. Found: C, 88.19; H, 6.73.

Treatment of o-duroylphenylphenylcarbinol with acid. A solution of 600 mg. (1.7 mmoles) of *o*-duroylphenylphenylcarbinol in 100 ml. of ether was shaken in a separatory funnel with an equal volume of 40% hydrochloric acid. The ether layer was washed with sodium bicarbonate solution, then with water, and dried over magnesium sulfate; the ether was removed on the concentrator. The yellow residue was recrystallized twice from absolute ethanol with Darco decolorization to give 450 mg. (83%) of 1-duryl-3-phenylisobenzofuran, m.p. 118–119°.

1-Duryl-3-(2-methoxyphenyl)isobenzofuran. To a solution of *o*-duroylphenyllithium in ether at −30° to −35°, prepared from 2.54 g. (0.008 mole) of *o*-duroylbromobenzene and 9.20 ml. of 0.87*N* *n*-butyllithium solution, was added all at once a solution of 1.09 g. (0.008 mole) of *o*-methoxybenzaldehyde in 15 ml. of dry ether. The resultant yellow-green reaction mixture was subsequently treated as in the procedure involving benzaldehyde. The yield was 0.86 g. (30%); the analytical sample melted at 127–128°. The infrared spectrum of this material is almost identical with that of 1-duryl-3-phenylisobenzofuran.

Anal. Calcd. for $C_{25}H_{24}O_2$: C, 84.23; H, 6.78. Found: C, 84.12; H, 6.69.

1-Duryl-3-(4-methoxyphenyl)isobenzofuran. By the method described in the preceding example, 1.09 g. (0.008 mole) of *p*-methoxybenzaldehyde was condensed with *o*-duroylphenyllithium; the lithium reagent was prepared from 2.54 g. (0.008 mole) of *o*-duroylbromobenzene and 9.41 ml. of 0.85*N* *n*-butyllithium solution, yield 1.05 g. (33%), m.p. 123–124°. The infrared spectrum was almost superimposable on that of 1-duryl-3-(2-methoxyphenyl)isobenzofuran.

Anal. Calcd. for $C_{25}H_{24}O_2$: C, 84.23; H, 6.78. Found: C, 84.10; H, 6.70.

1-Duryl-3-(2-chlorophenyl)isobenzofuran. A solution of 1.12 g. (0.008 mole) of *o*-chlorobenzaldehyde in 10 ml. of dry ether was added to an ethereal solution of *o*-duroylphenyllithium at −30° to −35°, prepared from 2.54 g. (0.008 mole) of *o*-duroylbromobenzene and 10.4 ml. of 0.75*N* *n*-butyllithium solution. The reaction mixture was treated as in the preceding example, yield 1.15 g. (40%); the pure compound melted at 131–132°. The spectral data are similar to those of the preceding examples.

Anal. Calcd. for $C_{24}H_{21}OCl$: C, 79.86; H, 5.88. Found: C, 80.01; H, 5.80.

1-Duryl-3-(4-chlorophenyl)isobenzofuran. A solution of *o*-duroylphenyllithium at −30° to −35° was prepared from 2.54 g. (0.008 mole) of *o*-duroylbromobenzene and 10.3 ml. of 0.78*N* *n*-butyllithium solution. The lithium reagent was condensed with *p*-chlorobenzaldehyde by the method described for *o*-chlorobenzaldehyde, yield 1.19 g. (41%); m.p. 129–130°. The infrared spectrum is almost superimposable on that of 1-duryl-3-(2-chlorophenyl)isobenzofuran.

Anal. Calcd. for $C_{24}H_{21}OCl$: C, 79.86; H, 5.88. Found: C, 79.71; H, 5.81.

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3-(*p*-Methoxyphenoxy)-2,6-dinitrobenzaldehyde and Two of Its Derivatives

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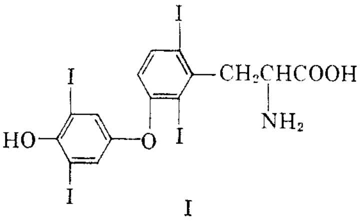
The present work was started for the purpose of testing the feasibility of the synthesis of the thyroxine analog (I) by starting with commercially available *m*-hydroxybenzaldehyde. The project will not be completed, but several intermediate nitro compounds have been prepared and it seems possible that the entire synthesis could be accomplished.



I

Two isomeric 3-hydroxydinitrobenzaldehydes, *viz.* 3-hydroxy-2,6-dinitrobenzaldehyde and 3-hydroxy-4,6-dinitrobenzaldehyde were prepared according to Hodgson and Beard[1] by nitration of 3-hydroxy-6-nitrobenzaldehyde.[2] It was advantageous to separate these two isomers by chromatography on Magnesol[3] rather than by fractional crystallization.

The reaction of *p*-toluenesulfonyl chloride with 3-hydroxy-2,6-dinitrobenzaldehyde yielded 3-(*p*-toluenesulfonyloxy)-2,6-dinitrobenzaldehyde which reacted with *p*-methoxyphenol in pyridine[4] to produce 3-(*p*-methoxyphenoxy)-2,6-dinitrobenzaldehyde. Reduction with aluminum isopropoxide gave 3-(*p*-methoxyphenoxy)-2,6-dinitrobenzyl alcohol. An attempt to prepare this compound by reaction of 3-(*p*-toluenesulfonyloxy)-2,6-dinitrobenzyl alcohol with *p*-methoxyphenol in pyridine was unsuccessful. Phosphorus pentachloride con-

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[6] The infrared spectra were determined by Mr. James Brader, Mr. Paul McMahan, Mrs. Mary Verkade, and Miss Charlene Leubke.

[7] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1958.

[8] The microanalyses were performed by Mr. Josef Nemeth, Miss Claire Higham, and Miss Jane Liu.

* Deceased.

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[2] R. Pschorr, *Ber.*, **34**, 4000 (1901); P. Friedlaender and O. Schench, *Ber.*, **47**, 3043 (1914).

[3] J. C. Colbert, D. W. Fox, and C. Matuszak, *J. Am. Chem. Soc.*, **77**, 2447 (1955).

[4] *Cf.* E. T. Burrows, J. C. Clayton, B. A. Hems, and A. G. Long, *J. Chem. Soc.*, S190 (1949).