TABLE II

Thiol Adducts (VI) from 2-Aralkylidene-3(2H)-thianaphthenone-1,1-dioxides (V)

Arylidene Deriv.	Thiol Adduct Ar′ =	Reaction Temp., °C.	M.p., °C.[a]	Yield, %	Solvent for Cryst.[c]	Color with H_2SO_4	Formula	Analysis % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Sulfur Found	Sulfur Calcd.
Vb	C_6H_5	100	116	85	A	Orange-red	$C_{22}H_{18}O_3S_2$	67.00	66.87	4.56	4.32	16.24	16.01
Vc	$C_6H_4CH_3$-*p*	130	156	82	B	Red	$C_{23}H_{20}O_3S_2$	67.65	67.24	4.90	4.73	15.69	15.31
	C_6H_5	120	155	79	B	Orange	$C_{22}H_{18}O_3S_2$	67.00	66.91	4.56	4.55	16.24	15.89
Vd	$C_6H_4CH_3$-*p*	130	182	76	B	Red	$C_{23}H_{20}O_3S_2$	67.65	65.67	4.90	4.84	15.69	15.56
	C_6H_5	100	137	92	B	Red	$C_{22}H_{18}O_3S_2$	67.00	66.69	4.56	4.41	16.24	15.90
Ve	$C_6H_4CH_3$-*p*	100	135	91	A	Red	$C_{23}H_{20}O_3S_2$	67.65	67.59	4.90	4.77	15.69	15.60
	C_6H_5	120	150	87	B	Yellow	$C_{21}H_{15}ClO_3S_2$[b]	60.79	60.81	3.61	3.42	15.44	15.19

[a] Melting points are uncorrected. [b] Calcd. for Cl: 8.56. Found: Cl, 8.32. [c] A, Benzene–petroleum ether (b.p. 50–70°). B, Benzene.

less crystals, m.p. 153° and identified as IIIa (melting point and mixed melting point).

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Studies on 3-Acylcatechols

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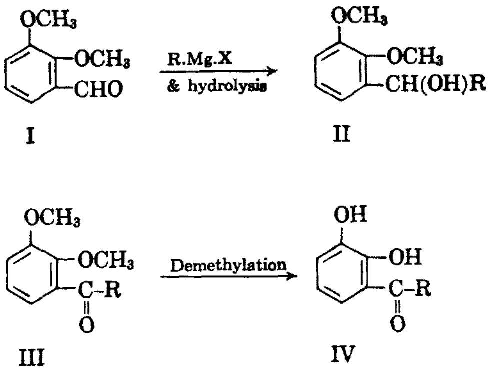
The methods available for the preparation of 3-acylcatechols, which are needed as starting materials in our work, are very limited. The most reliable method is that described by Krannichfeldt[1] for 2,3-dihydroxyacetophenone (IV, R = CH_3) according to the following scheme I–IV.



We have prepared 2,3-dihydroxypropiophenone (IV, R = C_2H_5) and 2,3-dihydroxybutyrophenone (IV, R = *n*-C_3H_7) according to the above scheme. These compounds are pale yellow in color, and give a green color with ferric chloride that changes to red by the addition of sodium carbonate solution, a characteristic color test for catechols.[2,3]

Miller, Hartung, Rock, and Crossley[4] referred to 2,3-dihydroxypropiophenone (IV, R = C_2H_5) as a by-product of the Fries rearrangement of the corresponding catechol diester. The melting point (102.5–103.5°) as reported by these authors[4] does not correspond to the melting point (53°) of the product which we have obtained. The position of the substituents in our products which are prepared by an orthodox method cannot be questioned. This leads us to doubt the correctness of the structure given to the by-product obtained by Miller *et al.*[4]

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(1) H. V. Krannichfeldt, *Ber.*, **46**, 4017, 4018 (1913).

(2) Compare Paul Karrer, *Organic Chemistry*, Fourth English Edition, Elsevier Publ. Co., Inc., New York, N. Y., p. 435.

(3) A. Schönberg, W. I. Awad and G. A. Mousa, *J. Am. Chem. Soc.*, **77**, 3850 (1955).

(4) Ellis Miller, Walter H. Hartung, Henry J. Rock, and Frank S. Crossley, *J. Am. Chem. Soc.*, **60**, 7 (1938).

On repeating the experiment described for the Fries rearrangement of catechol dipropionate, we were able to isolate a lower boiling fraction (at approximately the same temperature described in reference 4) and which possessed the same melting point (104–105°) as described by these authors. This product proved to be catechol by melting point and mixture melting point determinations. It is to be noticed that no analytical figures are given for this compound.[4]

EXPERIMENTAL[5]

Preparation of 2,3-dihydroxypropiophenone (IV, R = C_2H_5). (*a*) *Action of ethylmagnesium iodide on 2,3-dimethoxybenzaldehyde.* A solution of the aldehyde (I) (5 g.) in anhydrous ether was added dropwise to the ethylmagnesium iodide (from 6.5 g. ethyl iodide and 0.9 g. magnesium) while cooling in ice. When the addition was complete the reaction mixture was refluxed for 1 hr. and left to stand, at room temperature, overnight. After decomposition with dilute acetic acid and ice, the ethereal layer was shaken with sodium bisulfite solution and then with water. It was then dried (Na_2SO_4), the ether driven off, and the remaining oil distilled to give II (R = C_2H_5) as a colorless liquid, b.p. 108–110°/2 mm., yield 3.9 g.

(*b*) *Preparation of 2,3-dimethoxypropiophenone.* The previously described carbinol (3.5 g.) was added to a mixture of potassium dichromate (7 g.), water (35 ml.), and concentrated sulfuric acid (3.2 g.). The reaction mixture was immediately steam-distilled, and the distillate was extracted with ether, dried (Na_2SO_4), and then the ether was driven off. III (R = C_2H_5) was obtained as a colorless oil b.p. 114°/2 mm. yield 2.48 g.

The *2,4-dinitrophenylhydrazone* derivative was crystallized from ethyl acetate in reddish brown crystals m.p. 219°.

Anal. Calcd. for $C_{17}H_{18}O_6N_4$: N, 14.97. Found: N, 15.20.

The *semicarbazone* was crystallized from methyl alcohol in colorless crystals m.p. 188°.

Anal. Calcd. for $C_{12}H_{17}N_3O_3$; C, 57.35; H, 6.8; N, 16.7. Found: C, 57.39; H, 6.8; N, 16.56.

(*c*) *Demethylation of 2,3-dimethoxypropiophenone* (III, R = C_2H_5). The previously described ketone (III, R = C_2H_5) (2.8 g.) was refluxed with hydriodic acid (sp. gr. 1.96) (11 g.) and an equal volume of glacial acetic acid for 6 hr. The reaction mixture was then poured onto ice and left overnight. The precipitated product was filtered off, dissolved in benzene, and the dark solution treated with charcoal. To the filtrate after concentration, a few drops of petroleum ether (40–60°) were added, whereby 2,3-dihydroxypropiophenone separated out. It was recrystallized from petroleum ether (40–60°) in pale yellow crystals, m.p. 53°, yield 41%. It gave a green color with alcoholic ferric chloride solution which changed to red on the addition of sodium carbonate solution.

Anal. Calcd. for $C_9H_{10}O_3$: C, 65.1; H, 6.1. Found: C, 65.7; H, 6.2.

The *2,4-dinitrophenylhydrazone* derivative was crystallized from ethyl acetate m.p. 229°.

Anal. Calcd. for $C_{15}H_{14}O_6N_4$: N, 16.2. Found: N, 15.7.

Prepuration of 2,3-dihydroxybutyrophenone (IV, R = n-C_3H_7). (*i*). *Action of propylmagnesium iodide on 2,3-dimethoxybenzaldehyde.* A solution of the aldehyde (I) (5 g.) in anhydrous ether was added dropwise to propylmagnesium iodide (from 6.2 g. propyl iodide and 0.9 g. magnesium) while cooling in ice. The reaction mixture was treated as in (*a*) and the carbinol (II, R = n-C_3H_7) was obtained as a colorless liquid, yield 3.5 g.

Its *phenylurethane* derivative was crystallized from petroleum ether (60–80°) m.p. 130°.

Anal. Calcd. for $C_{19}H_{23}O_4N$: C, 69.3; H, 7.0; N, 4.25. Found: C, 69.4; H, 7.2; N, 4.4.

(*ii*). *Preparation of 2,3-dimethoxybutyrophenone* (III, R = n-C_3H_7). The above carbinol (II, R = n-C_3H_7) (3.5 g.) was oxidized as previously described in (*b*). It was obtained as a colorless liquid, b.p. 112–113°/0.6 mm., yield 2.5 g.

The *semicarbazone* was crystallized from ethyl alcohol in colorless crystals m.p. 153.5°.

Anal. Calcd. for $C_{13}H_{19}N_3O_3$: N, 15.84; Found: N, 15.99.

(*iii*). *Demethylation of 2,3-dimethoxybutyrophenone.* This ketone (2.1 g.) was similarly treated as in (*c*) to give 2,3-dihydroxybutyrophenone (IV, R = n-C_3H_7) in pale yellow crystals, "from petroleum ether (60–80°)" m.p. 61°, yield, 0.7 g. It gave a bluish green color with alcoholic ferric chloride solution which turned reddish brown on adding sodium carbonate solution.

Anal. Calcd. for $C_{10}H_{12}O_3$: C, 66.65; H, 6.7. Found: C, 66.5; H, 6.8.

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[5] Microanalyses were carried out by Alfred Bernhardt, Germany. Melting points are not corrected.

A Note on the Mode of Addition of Phenyllithium to Phenanthrenequinone Monoxime

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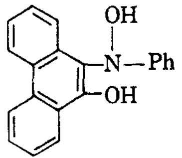
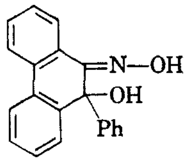
Mustafa *et al.*[1] claimed that phenanthrenequinone monoxime reacts with phenyllithium by 1,4-addition to give 10-phenylhydroxylamino-9-hydroxyphenanthrene (I).



I



II

The main line of evidence upon which these authors assigned the above structure is that they obtained the same compound (I) by the action of phenylmagnesium bromide on the same oxime,[2] and they verified the identity of the two products by a mixture melting point experiment.

We have proved[3] that the mode of addition of phenylmagnesium bromide to phenanthrenequinone monoxime is 1,2-addition, thus produicng 9-phenyl-9,10-dihydro-10- oximino-9-hydroxyphenanthrene (II). We have now found that when phenyllithium is allowed to react with phenanthrenequinone monoxime, under the same conditions

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[1] A. Mustafa, W. Asker, O. H. Hishmat, A. F. A. Shalaby, and M. Kamel, *J. Am. Chem. Soc.*, **76**, 5447 (1954).

[2] A. Mustafa and M. Kamel, *J. Am. Chem. Soc.*, **76**, 124 (1954).

[3] W. I. Awad and A. R. A. Raouf, *J. Org. Chem.*, **23**, 282 (1958).