1,6-Dimethyl-4-isopropyl-6-hydroxy-$\Delta^{5,10}$-octalin (III).—A solution of II (15 g.) in dry ether was gradually added to a solution of methylmagnesium iodide from methyl iodide (12.4 g.) and magnesium (2.1 g.), a vigorous reaction occurring. The mixture was then gently refluxed for ninety minutes, cooled and poured into a mixture of cracked ice and ammonium chloride solution. The ether layer was removed and the aqueous layer extracted with ether several times. The solvent was removed from the united ether extracts after drying and the residual oil distilled *in vacuo*. A fraction (10.2 g., 63%) b. p. 110–114° (1 mm.) (bath temperature 160°) was collected.

Anal. Calcd. for $C_{15}H_{26}O$: C, 81.1; H, 11.7. Found: C, 81.0; H, 11.8.

1,6-Dimethyl-4-isopropylnaphthalene (Cadalene, IV).—A mixture of III (6 g.) and powdered sulfur (2.7 g.) was heated for four hours at 200–250° in an oil-bath. The resultant very dark product was distilled with steam, the cadalene coming over as a yellow-brown oil which was collected and dried in ether and eventually distilled *in vacuo*, being thus obtained as a pale yellow oil (4.8 g., 81%) b. p. 163–164° (18 mm.) (literature,[5] b. p. 157–158° (12 mm.)). The picrate formed orange needles (from ethanol) m. p. 116° (literature,[2] m. p. 114–116°).

Anal. Calcd. for $C_{21}H_{21}O_7N_3$: N, 9.8. Found: N, 10.1.

The trinitrotoluate formed yellow needles (from methanol) m. p. 82.5° (literature,[6] m. p. 83°).

Anal. Calcd. for $C_{22}H_{23}O_6N_3$: N, 9.9. Found: N, 9.9.

Acknowledgment.—We are indebted to Miss Joyce Fildes for the combustion micro-analyses recorded in this paper.

Summary

A convenient, relatively high-yielding synthesis of cadalene from l-menthone involving use of the Mannich reaction is described.

(5) Ruzicka and Meyer, *Helv. Chim. Acta*, **4**, 508 (1921).

(6) Briggs and Taylor, THIS JOURNAL, **69**, 716 (1947).

SYDNEY, AUSTRALIA RECEIVED JULY 5, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

Some Addition Reactions of Chalcones. I. The Preparation of Some γ-Ketosulfones

BY HENRY GILMAN AND LOUIS F. CASON

In connection with the search for new chemotherapeutic agents[1] we prepared a number of γ-ketosulfones by means of the addition of sulfinic acids to chalcones.

$$RCH{=}CHCOR' + R''SO_2H \longrightarrow RCH(SO_2R'')CH_2COR'$$

R, R′, R″ are aromatic

The 1,4-addition of certain sulfur compounds and other unsymmetrical reagents to chalcones has been known since the rather early development of the chemistry of conjugated systems. Posner[2] treated thiols with benzalacetophenone in the presence of hydrogen chloride and/or zinc chloride in ethanol or acetic acid. The products were trialkylmercapto derivatives of 1,3-diphenylpropane resulting from the addition of one molecule of the thiol to the α,β-unsaturated linkage and the condensation of two molecules with the carbonyl group of the ketone. These compounds generally lost two molecules of the thiol upon oxidation and were converted into the corresponding γ-ketosulfone. From benzenethiol and the ketone, however, there was obtained only the 1,4-addition product which readily underwent oxidation to the ketosulfone identical with that obtained from the addition of benzenesulfinic acid to benzalacetophenone.[3] Later Ruhemann[4] showed that thiols undergo 1,4-addition to chalcones in the presence of the basic catalysts piperidine or sodium methoxide. In more recent studies, Nicolet[5] showed that these addition reactions are reversible, the equilibrium being shifted far to the left in the presence of alkalies. He demonstrated that *p*-toluenethiol and α-toluenethiol add smoothly to chalcone without the aid of a catalyst.[6] Gilman and King[7] obtained identical products by the addition and subsequent hydrolysis of *p*-tolylthiomagnesium iodide to benzalacetophenone. In some later investigations, γ-ketosulfides have been prepared in excellent yields from chalcones and aliphatic thiols.[8]

γ-Ketosulfones have been previously prepared by the 1,4-addition of sulfinic acids to chalcones[3,9,10a,10b] and from the interaction of aromatic hydrocarbons and sulfur dioxide with chalcones in the presence of anhydrous aluminum chloride.[11] According to Kohler and Reimer,[9] the products are crystalline and stable under ordinary conditions but are decomposed by bases. Addition products of this type have been used to identify small amounts of sulfinic acids obtained from the cleavage and rearrangement of certain sulfones.[10a]

Several new chalcones and related α,β-unsaturated ketones (listed in Table I) were prepared as intermediates in this study by the known procedures of Claisen,[12] and of Kohler and

(1) Gilman and Broadbent, THIS JOURNAL, **69**, 2053 (1947), mention several important sulfones and related compounds which have shown promise in antituberculous and antimalarial tests.

(2) Posner, *Ber.*, **34**, 1395 (1901).

(3) Posner, *ibid.*, **35**, 799 (1902).

(4) Ruhemann, *J. Chem. Soc.*, **87**, 17, 461 (1905).

(5) Nicolet, THIS JOURNAL, **53**, 3066 (1931).

(6) Nicolet, *ibid.*, **57**, 1098 (1935).

(7) Gilman and King, *ibid.*, **47**, 1136 (1925).

(8) Frank and Smith, *ibid.*, **68**, 2103 (1946); Frank, Drake, Smith and Stevens, *J. Polymer Sci.*, **3**, 50 (1948) [*C. A.*, **42**, 4385 (1948)]; Kipnis and Ornfelt, THIS JOURNAL, **71**, 3554 (1949).

(9) Kohler and Reimer, *Am. Chem. J.*, **31**, 163 (1904).

(10) (a) Martin, *Iowa State Coll. J. Sci.*, **21**, 38 (1946) [*C. A.*, **41**, 952 (1947)]; (b) Goldberg, Hein mann, and Grier, *Jubilee Vol. Emil Barell*, 341 (1946) [*C. A.*, **41**, 4153 (1947)].

(11) Vorländer and Friedberg, *Ber.*, **56**, 1144 (1923).

(12) Claisen, *ibid.*, **20**, 657 (1887).

TABLE I

α,β-UNSATURATED KETONES, RCH=CHCOR'

No.	R	R'	M. p., °C.[a]	Yield, %	Formula	Analyses, %[b] Calcd.	Found
1	2-Quinolyl	*p*-Methoxyphenyl	133–134[c]	88	$C_{19}H_{15}O_2N$	N, 4.84	4.61
2	2-Quinolyl	*p*-Chlorophenyl	165	30[d,e]	$C_{18}H_{12}ONCl$	Cl, 11.94	11.89
3	2-Quinolyl	4-Quinolyl	188[f]	65	$C_{21}H_{14}ON_2$	N, 9.03	9.25
4	Phenyl	2-Dibenzothienyl	154–155	62[g,h]	$C_{21}H_{14}OS$	S, 10.18	10.04
5	*p*-Dimethylaminophenyl	2-Dibenzothienyl	163–164	57[g]	$C_{23}H_{19}ONS$	S, 8.96	9.02
6	*m*-Nitrophenyl	*p*-Acetamidophenyl	210	80	$C_{17}H_{14}O_4N_2$	N 9.03	9.16
7	*m*-Nitrophenyl	2-Pyridyl	178[i]	96	$C_{14}H_{10}O_3N_2$	N, 11.03	11.30
8	*m*-Aminophenyl	*p*-Aminophenyl	168–169	68[j]	$C_{15}H_{14}ON_2$	N, 11.77	11.94

[a] All melting points are uncorrected. [b] The analyses for nitrogen were made by the micro Dumas method. Those for sulfur and chlorine were performed with a macro Parr bomb. [c] Unless otherwise stated absolute ethanol was the solvent employed in recrystallization. [d] Secondary condensation products were formed. [e] The product was recrystallized from a 50% mixture of ethanol and ethyl acetate. [f] The product was purified by digesting with ethyl acetate. [g] In preparing these compounds it was necessary to warm the reaction to 40°. The products were separated from oils. [h] The product was recrystallized from ethyl acetate. [i] The crude condensation product was filtered and washed with methanol. [j] Prepared by the reduction and hydrolysis of No. 6 with stannous chloride and hydrochlorice acid.

TABLE II

γ-KETOSULFONES, RCH(SO_2R'')CH_2COR'

No.	R	R'	R''	M. p., °C.[a]	Yield, %	Formula	S Analyses,[b] % Calcd.	Found	
1	*p*-Anisyl	*p*-Chlorophenyl	*p*-Tolyl	158[c]	72	$C_{23}H_{21}O_4ClS$	7.50	7.45	
2	*p*-Dimethylaminophenyl	*p*-Chlorophenyl	*p*-Tolyl	153–156	53	$C_{24}H_{24}O_3NClS$	7.02	7.30	
3	*p*-Dimethylaminophenyl	*p*-Anisyl	*p*-Tolyl	149	30	$C_{25}H_{27}O_4NS$	7.32	7.34	
4	Phenyl	Phenyl	*p*-Acetamidophenyl	176–178	80	$C_{23}H_{21}O_4NS$	7.85[d]	7.85	
5	*p*-Anisyl	*p*-Chlorophenyl	*p*-Acetamidophenyl	159–160	71	$C_{24}H_{22}O_5NClS$	6.79[e]	6.75	
6	Phenyl	2-Pyridyl	*p*-Tolyl	172–174	86	$C_{21}H_{19}O_3NS$	8.75[f]	8.40	
7	*o*-Chlorophenyl	*p*-Anisyl	*p*-Acetamidophenyl	160–161[g]	81	$C_{24}H_{23}O_5NClS$	6.78	6.46	
8	3,4-Methylenedioxyphenyl	Phenyl	*p*-Acetamidophenyl	150–153[h]	69	$C_{24}H_{21}O_6NS$	7.10	7.32	
9	Phenyl	2-Dibenzothienyl	*p*-Tolyl	180–182	68	$C_{28}H_{22}O_4S_2$	13.66	12.86	12.75[i]
10	Phenyl	2-Dibenzothienyl	3-Acetamido-4-methoxyphenyl	175–177	56	$C_{30}H_{25}O_5NS_2$	11.80	11.50	
11	*p*-Dimethylaminophenyl	*p*-Anisyl	*p*-Acetamidophenyl	155–156	42	$C_{26}H_{28}O_6N_2S$	6.67	6.65	
12	*p*-Dimethylaminophenyl	*p*-Chlorophenyl	*p*-Acetamidophenyl	158[j]	32	$C_{25}H_{25}O_4N_2ClS$	6.61	6.66	
13	3,4-Methylenedioxyphenyl	Phenyl	*p*-Tolyl	145–148	41	$C_{23}H_{20}O_6S$	7.84	7.73	
14	*o*-Chlorophenyl	*p*-Anisyl	*p*-Tolyl	149–150	83	$C_{23}H_{21}O_4ClS$	7.47	7.20	
15	Phenyl	Phenyl	*p*-Chlorophenyl	175–176	89	$C_{21}H_{17}O_3ClS$	8.31	8.26	
16	Phenyl	Phenyl	3-Chloro-4-methoxyphenyl	172–174	94	$C_{22}H_{19}O_4ClS$	7.72	7.75	
17	Phenyl	Phenyl	3-Acetamido-4-methoxyphenyl	155–156	39	$C_{24}H_{23}O_5NS$	7.32	7.38	
18	*p*-Dimethylaminophenyl	*p*-Anisyl	*p*-Chlorophenyl	149–150	45	$C_{24}H_{24}O_4NClS$	7.00	7.06	
19	*p*-Dimethylaminophenyl	*p*-Chlorophenyl	3-Acetamido-4-methoxyphenyl	176	39	$C_{26}H_{27}O_5N_2ClS$	6.24	6.33	
20	2-Quinolyl	*p*-Anisyl	*p*-Acetamidophenyl	170–172[g]	53	$C_{27}H_{24}O_5N_2S$	6.56	6.81	
21	2-Quinolyl	*p*-Anisyl	*p*-Chlorophenyl	158–160[g]	64	$C_{25}H_{20}O_4NClS$	6.88	6.83	
22	2-Quinolyl	*p*-Anisyl	Phenyl	150–152	59	$C_{25}H_{21}O_4NS$	7.42	7.00	
23	2-Quinolyl	*p*-Anisyl	*p*-Isopropylphenyl	156–158	73	$C_{28}H_{27}O_4NS$	6.76	6.57	
24	Phenyl	Phenyl	*p*-Dimethylaminophenyl	191–192	20[k]	$C_{23}H_{23}O_3NS$	8.14	8.12	
25	*m*-Aminophenyl	*p*-Aminophenyl	*p*-Tolyl	184–185	70	$C_{21}H_{22}O_3N_2S$	8.38	8.12	
26	*m*-Aminophenyl	*p*-Aminophenyl	*p*-Acetamidophenyl	186–200	77	$C_{23}H_{23}O_4N_3S$	7.32	7.39	
27	Phenyl	Phenyl	*p*-Isopropylphenyl	157–158	65	$C_{24}H_{24}O_4S$	8.20	8.57	
28	*o*-Chlorophenyl	*p*-Anisyl	*p*-Isopropylphenyl	150	17	$C_{25}H_{25}O_4ClS$	7.02	7.14	
29	Phenyl	*p*-Chlorophenyl	*p*-Tolyl	188	60	$C_{22}H_{19}O_3ClS$	8.04	8.03	
30	*m*-Nitrophenyl	2-Pyridyl	*p*-Isopropylphenyl	170–172	57	$C_{23}H_{21}O_5N_3S$	7.16	6.2	6.21[l]

[a] The melting points are uncorrected. All of the compounds listed above decomposed at their melting points. [b] See note (*b*) Table I. [c] Unless otherwise stated the pure product was obtained by recrystallization from ethyl acetate or from a mixture of ethanol and ethyl acetate or from an ethyl acetate–acetic acid solution. [d] Calcd. for $C_{23}H_{21}O_4NS$: N, 3.44. Found: N, 3.59. [e] Calcd. for $C_{24}H_{22}O_5NClS$: N, 2.97; Cl, 7.5. Found: N, 3.16; Cl, 7.2 and 7.3. [f] Calcd. for $C_{21}H_{19}O_3NS$: N, 4.06. Found: N, 4.02. [g] Purified by digesting with hot ethanol. [h] Recrystallized from glacial acetic acid. [i] Several recrystallizations from glacial acetic acid and subsequent drying *in vacuo* did not increase the purity of the compound. [j] This sulfone was purified by digesting with ethyl acetate. [k] The addition product formed after allowing the reaction to stand at room temperature for two weeks. The product sintered at 177° but decomposed sharply at 191–192°. [l] Repeated recrystallization of the crude product from ethyl acetate and subsequent drying *in vacuo* did not increase its melting point or analytical purity. The per cent. of sulfur in this compound corresponded to that calculated for the acetate. Calcd. for $C_{23}H_{21}O_5N_2S\cdot CH_3COOH$: S, 6.45. Found: S, 6.2 and 6.21.

Chadwell.[13] The intermediate sulfinic acids were secured by the conventional reduction of the corresponding arylsulfonyl chloride with aqueous sodium sulfite.[14] Lithium *p*-dimethylaminobenzenesulfinate and lithium benzenesulfinate, however, were prepared in yields of 76 and 74%,

(13) Kohler and Chadwell, "Org. Syn.," Coll. Vol. I, 78 (1941).

(14) Smiles and Bere, *ibid.*, 7 (1941).

respectively, by passing anhydrous sulfur dioxide into ethereal solutions of the respective aryllithium compounds.

The γ-ketosulfones were prepared in good yields (Table II) by one of three procedures: (1) The free sulfinic acid was liberated from its sodium salt by neutralization with the calculated amount of concentrated hydrochloric acid. The sodium chloride was filtered from the solution and the filtrate added immediately to an ethanolic solution of the chalcone. (2) A suspension of the alkali sulfinate and chalcone in ethanol was warmed with shaking with a slight excess of glacial acetic acid until homogeneous solution was obtained. (3) Equimolar quantities of the alkali sulfinate and the chalcone were warmed in an excess of glacial acetic acid until completely dissolved. Generally the addition product crystallized from the solution upon cooling or after standing at room temperature for one-half hour. These products were on the whole difficultly soluble in ethanol but were easily recrystallized from ethyl acetate, acetic acid or a mixture of the two solvents. Without exception, they decomposed sharply at their melting points.

Rather low yields of the γ-ketosulfone resulted when the unsaturated ketones contained basic constituents. In two reactions involving the addition of thiols to chalcones, *p*-thiocresol formed an addition product with 4-dimethylamino-4′-chlorochalcone after refluxing in ethanol for twelve hours, while quinoline-2-thiol failed to add to benzalacetophenone. In these instances it is entirely possible that the ease of addition of the sulfinic acid or thiol to the unsaturated molecule may be subject to slight reversal because of the basic nature of the substituent. In a similar reaction in which β-diethylaminoethanethiol was treated with benzalacetophenone, it was observed that the free base did not undergo 1,4-addition.[15] The addition product was obtained, however, when the corresponding amine hydrochloride was used. The conversion of the γ-ketosulfide amine hydrochloride to the free base was complicated by the reversible nature of the reaction.

Acknowledgment.—The authors are grateful to Parke, Davis and Company for arranging for the tests.

Experimental

1-(4-Methoxyphenyl)-3-(2-quinolyl)-2-propen-1-one.—The procedure which follows is typical of the preparation of all of the α,β-unsaturated ketones listed in Table I. To a solution of 15.7 g. (0.1 mole) of 2-quinolinealdehyde[16] and 14 g. (0.1 mole) of *p*-methoxyacetophenone in 60 ml. of absolute ethanol there was gradually added with shaking 10 ml. of a 10% solution of sodium methoxide in methanol. The condensation took place immediately, and the light yellow crystalline product was separated by filtration, washed with dilute ethanol, and recrystallized from ethanol. Twenty-four and five-tenths grams (88%) of the pure product was obtained; m. p. 133–134°.

Sodium *p*-Isopropylbenzenesulfinate.—*p*-Isopropylbenzenesulfonyl chloride was prepared from 120 g. (1.0 mole) of isopropylbenzene by the method of Huntress and Autenrieth[17a] as modified by Gilman and Broadbent.[17b] The crude product was reduced with aqueous sodium sulfite according to the general procedure described by Smiles and Bere.[14] The product was isolated as the sodium salt. Forty-four and five-tenths grams (24%) was obtained.

Anal. Calcd. for $C_9H_{11}O_2SNa \cdot 2H_2O$: S, 13.22. Found: S, 13.00.

2-Chloroanisole-4-sulfinic Acid.—Fifty-seven and one-tenth grams (0.24 mole) of 2-chloroanisole-4-sulfonyl chloride[18] was reduced by 126 g. (0.5 mole) of sodium sulfite ($Na_2SO_3 \cdot 7H_2O$) in 500 ml. of water. The yield of the pure sulfinic acid was 38 g. (76%); the product softened to an opaque glass at 99–100° but melted sharply to a clear green liquid at 110–111°.

Anal. Calcd. for $C_7H_7O_3ClS$: S, 15.48. Found: S, 15.25,

Preparation of the γ-Ketosulfones: Procedure A.—A slight excess over the calculated amount of concentrated hydrochloric acid was added to a suspension of the finely pulverized sodium sulfinate in ethanol. After shaking vigorously, the sodium chloride was removed by filtration, and the filtrate immediately added to the equivalent amount of the chalcone dissolved in ethanol.[10a]

Procedure B.—Equimolar quantitites of the chalcone and the alkali sulfinate were suspended in from 50 to 60 ml. of absolute ethanol. A slight excess of glacial acetic acid was then added and the mixture warmed or shaken until a uniform solution was obtained.

Procedure C.—In the case of unsaturated ketones which were difficultly soluble in ethanol the reaction was carried out according to Procedure B except that glacial acetic acid was used as the solvent.

By the use of any of the methods described above, the addition product crystallized from the solution immediately or upon standing at room temperature for a few minutes. The pure products were obtained by recrystallization from ethyl acetate, acetic acid, or a mixture of these solvents.

Lithium *p*-Dimethylaminobenzenesulfinate.—Into an ethereal solution of *p*-dimethylaminophenyllithium prepared from 16 g. (0.08 mole) of *p*-bromodimethylaniline and 1.2 g. (0.16 g. atom) of lithium[19] there was passed anhydrous sulfur dioxide until Color Test I[20] for the organometallic compound was negative. The light green precipitate formed was removed by filtration, washed with ether, and dried. From this reaction there was obtained 11.6 g. (75%) of the crude sulfinate. From 5 g. (0.026 mole) of this product and 5 g. (0.024 mole) of benzalacetophenone there was obtained 2 g. (20%) of the corresponding γ-ketosulfone (Procedure B); m. p. 191–192° (dec.).

Anal. Calcd. for $C_{23}H_{23}O_3NS$: S, 8.14. Found: S, 7.99 and 8.24.

***p*-Chloro-β-(*p*-dimethylaminophenyl)-β-(*p*-tolylmercapto)-propiophenone.**—A solution of 2.9 g. (0.01 mole) of 4-dimethylamino-4′-chlorochalcone,[21] 1.2 g. (0.01 mole) of *p*-thiocresol, and five drops of piperidine in 50 ml. of ethanol was refluxed under nitrogen for twelve hours. The ethanol-insoluble addition product was separated and recrystallized from ethyl acetate. The yield of the pure product was 2.9 g. (70%); m. p. 148–149°.

Anal. Calcd. for $C_{24}H_{24}ONClS$: S, 7.83. Found: S, 7.82.

(15) L. Fullhart, *Iowa State Coll. J. Sci.*, **22**, 27 (1947) [*C. A.*, **42**, 1907 (1948)].

(16) Kaplan, THIS JOURNAL, **63**, 2654 (1941).

(17) (a) Huntress and Autenrieth, *ibid.*, **63**, 3446 (1941); (b) Gilman and Broadbent, *ibid.*, **69**, 2053 (1947).

(18) Child, *J. Chem. Soc.*, 715 (1932).

(19) Stuckwisch, *Iowa State Coll. J. Sci.*, **18**, 92 (1943) [*C. A.*, **38**, 728 (1944)].

(20) Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925).

(21) Pfeiffer and Kleu, *Ber.*, **66**, 1704 (1933).

Summary

The preparation of some γ-ketosulfones by means of the 1,4-addition of sulfinic acids to chalcones is described. Some new α,β-unsaturated ketones and sulfinic acids prepared as intermediate compounds in these reactions are reported.

AMES, IOWA RECEIVED DECEMBER 12, 1949

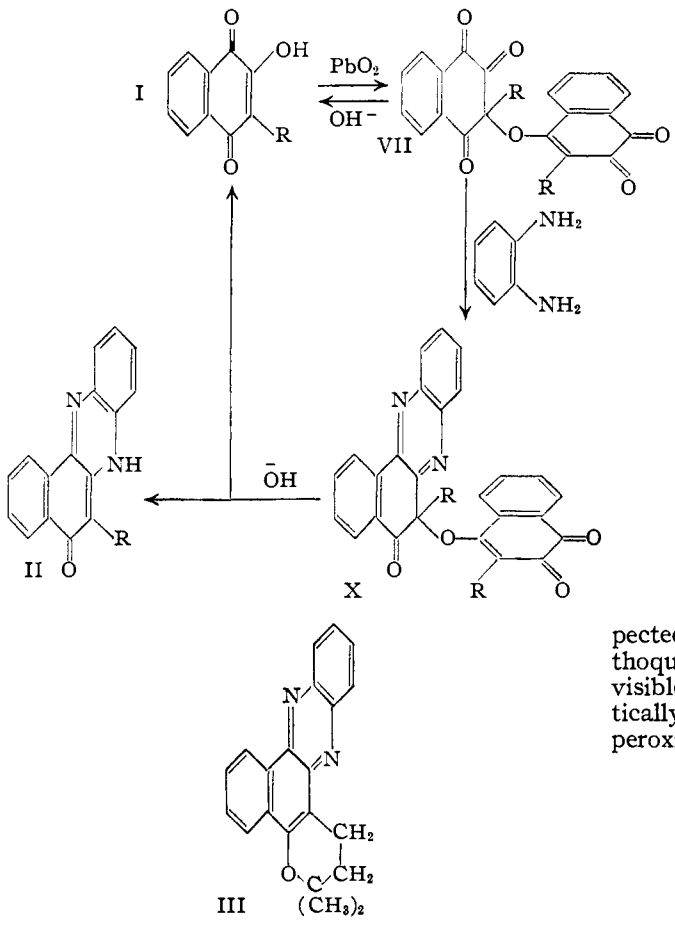
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

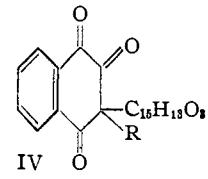
Hydroxynaphthoquinones. III. The Structure of Lapachol Peroxide

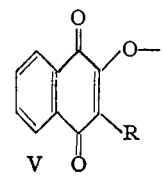
BY MARTIN G. ETTLINGER[1]

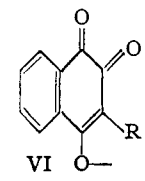
During studies on the natural pigment lapachol (I, R = $CH_2CH{=}C(CH_3)_2$), Hooker discovered[2] that this substance was oxidized by lead dioxide in acetic acid to a neutral, yellow compound of molecular formula $C_{30}H_{26}O_6$ equivalent to two molecules of lapachol less two atoms of hydrogen, which was named lapachol peroxide. A similar, unanalyzed product was obtained from 2-hydroxy-3-*n*-amyl-1,4-naphthoquinone (I, R = $(CH_2)_4CH_3$). Hooker observed that lapachol peroxide was reconverted to lapachol by alkaline hydrolysis in a molar yield of 1.6, but examined the peroxide no further and merely represented it graphically as containing an oxygen–oxygen bond.

In the present investigation, it was found that lapachol peroxide reacted easily with *o*-phenylenediamine in acetic acid to form a yellow, sparingly soluble *monophenazine*, $C_{36}H_{30}O_4N_2$, m. p. 185–186° (dec.). The monophenazine is cleaved by zinc and alkali to lapachol and lapeurhodone[3] (II, R = $CH_2CH{=}C(CH_3)_2$). The ultraviolet absorption spectrum (Fig. 1) of the phenazine resembles that of the peroxide (Fig. 2) and entirely lacks the intense bands at 305 mμ and 410–440 mμ in the spectrum (Fig. 1) of lapazine[3] (III). Therefore, one of the lapachol residues in the peroxide must contain a non-quinonoid 1,2-diketone group, which is possible in stable form only in the partial formula IV (R = $CH_2CH{=}CH(CH_3)_2$). Inasmuch as the peroxide is readily hydrolyzed in high yield to lapachol, the residues must be united by a carbon–oxygen bond and the group $C_{15}H_{13}O_3$ in IV is V or VI (R = $CH_2CH{=}C(CH_3)_2$). Since the 1,2,4-triketotetralin group in IV may be expected, similarly to benzil[4] or 2-methyl-1,4-naphthoquinone oxide,[5] to absorb only weakly in the visible, the band beyond 400 mμ that occurs practically identically in the spectra of lapachol peroxide and its phenazine must belong to V or VI.









(1) Member of the Society of Fellows, Harvard University.
(2) Hooker, THIS JOURNAL, **58**, 1168 (1936).
(3) Hooker, *ibid.*, **58**, 1190 (1936).
(4) Leonard and Blout, *ibid.*, **72**, 484 (1950).
(5) Fieser and Fieser, *ibid.*, **70**, 3215 (1948).