Anal. Calcd. for $C_{18}H_{14}OS$: C, 77.8; H, 5.08; S, 11.5. Found: C, 77.9; H, 5.27; S, 11.7.

2,4-Difurfurylidene-3-ketotetrahydrothiophene (XVIII, R = C_4H_3O).—Under the conditions described above for the analogous dibenzylidene derivative, 0.3 g. of 3-ketotetrahydrothiophene yielded on treatment with furfural (1.0 g.) the difurfurylidene derivative (0.75 g.); the brick red needles from glacial acetic acid gave a m. p. 193°.

Anal. Calcd. for $C_{14}H_{10}O_3S$: C, 65.1; H, 3.88. Found: C, 65.1; H, 4.16.

Summary

The Dieckmann cyclization of α,β'-dicarbomethoxymethylethyl sulfide under two different sets of experimental conditions has been shown to result in the formation of two different cyclic β-keto-esters, namely, 4-carbomethoxy-3-ketotetrahydrothiophene and 2-carbomethoxy-3-ketotetrahydrothiophene.

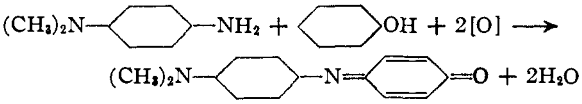
CAMBRIDGE, MASS. RECEIVED JUNE 17, 1946

[COMMUNICATION NO. 1091 FROM THE KODAK RESEARCH LABORATORIES]

Indoaniline Dyes. I. Some Phenol Blue Derivatives with Substituents in the Phenol Ring

BY PAUL W. VITTUM AND GORDON H. BROWN

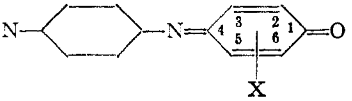
The indoaniline dyes have received little attention in recent years because their usefulness is limited by a general instability.[1] With their increasing use[2] as cyan dye images in color photography, however, a more complete examination of these and related dyes is now of interest. This paper describes the preparation and properties of a selected group of indoaniline dyes related to the simple dye, Phenol Blue, but having substituents in the phenol ring.



Phenol Blue has been prepared most conveniently by oxidizing an alkaline solution of *p*-aminodimethylaniline and phenol. The reaction has been reported to be effected by various oxidizing agents: potassium dichromate,[3,4] potassium ferricyanide,[3] potassium permanganate[3] and sodium hypochlorite.[5,6,7] Of these, the last reagent, as used in the procedure of Fieser and Thompson,[7] proved the most satisfactory for the preparation of the substituted dyes, but in some cases the phenol was attacked by the hypochlorite, leading to side products which made the isolation of the pure dye very difficult or impossible. The search for a more satisfactory procedure led to an adaptation of the photographic process of color development[2] which could be used to great advantage. In this procedure, the oxidizing agent was *silver chloride*, which was found to react readily with the *p*-phenylenediamine without attacking the phenols. The dyes prepared from *p*-aminodimethylaniline and the substituted phenols are listed in Table I.

TABLE I

PHYSICAL PROPERTIES OF DYES:



Substituent, X	M. p., °C.[a]	Crystallized from	Appearance of crystals	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
-H	161–162[b]	Ethanol	Dark purple needles	74.34	74.29	6.19	6.21	12.39	12.54
2-CH_3	123–124[c]	Ligroin	Dark purple crystals, green reflection	75.00	74.83	6.67	6.78	11.67	11.86
3-CH_3	118–119[d]	Ligroin	Black metallic crystals, gold reflection	75.00	74.84	6.67	6.54	11.67	11.85
2-Cl	125 (dec.)[e]	*n*-Butanol	Lustrous dark green needles	64.49	64.58	4.99	5.10	10.75	10.87
3-Cl	144–145[f]	Carbon tetrachloride	Dark purple metallic needles	64.49	64.28	4.99	4.64	10.75	10.67
2-Br	119–120 (dec.)	*n*-Butanol	Fine dark blue needles, green reflection	55.10	55.29	4.26	4.10	9.18	9.25
2-OCH_3	167–168	Ethanol	Dark purple crystals	70.31	70.02	6.25	6.38	10.94	10.74
3-OCH_3	141–142[f]	Ligroin	Purple-black crystals	70.31	70.25	6.25	6.16	10.94	10.86
2-$NHCOCH_3$	184–185	Ethanol	Dark golden needles	67.84	67.72	6.01	6.08	14.84	14.91
3-$NHCOCH_3$	150–151	Ethanol	Gold crystals	67.84	67.85	6.01	5.65	14.84	14.80
2-CH_2OH	157–158	*n*-Butanol	Dark purple crystals	70.31	70.29	6.25	6.40	10.94	10.91
2-$CH{=}CHCOC_6H_5$	158–159	Ethyl acetate	Fine green needles	77.53	77.24	5.62	5.41	7.87	7.93

[a] Melting points determined with Fisher–Johns apparatus. [b] Fieser[7] gives 161° from ethyl acetate; Heller,[6] 167° from alcohol; and Gnehm, 160° from ethyl acetate. [c] Fieser[7] gives 127°; Bayrac[4] gives 123°. [d] Fieser[7] gives 121°; Bayrac[4] gives 117–118°. [e] Bayrac[4] gives 125–126°. [f] Fieser[7] was unable to crystallize. Isolated as leuco form.

---

(1) See, for example, Bucherer, "Lehrbuch der Farbenchemie," O. Spamer, Leipzig, 1914, p. 293.

(2) R. Fischer, U. S. Patent 1,102,028 (1914), and many more recent patents.

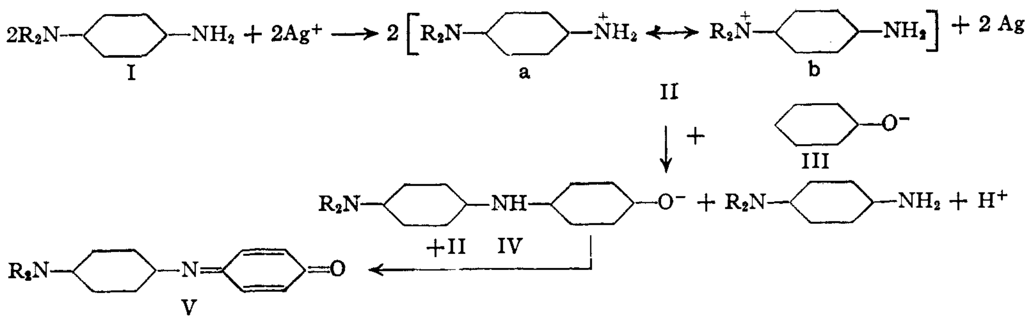
(3) Koechlin and Witt, German Patent 15,915 (1881).

(4) Bayrac, *Ann. chim.*, [7] **10**, 18 (1897).

(5) Gnehm, *J. prakt. Chem.*, **69**, 162 (1904).

(6) Heller, *Ann.*, **392**, 16 (1912).

(7) Fieser and Thompson, THIS JOURNAL, **61**, 376 (1939).



Attempts to prepare the dyes from 2,6-dichlorophenol, 2,6-dibromophenol and *o*-(N-methylacetamino)-phenol were unsuccessful. Dye formation was observed to occur, but the dyes were too unstable to permit isolation. *o*-Hydroxyacetophenone, ethyl salicylate, salicylamide, and salicylaldoxime also failed to yield dyes. With these phenols, each with an *o*-carbonyl or –CH=N–group, little or no dye formation appeared to take place.

The mechanism of the dye formation reaction probably involves,[8] first, an oxidation of the diamine (I) to a semiquinone ion, which is stabilized by the resonance IIa $\leftrightarrow$ IIb,[9] and which reacts with the phenolate ion (III) to yield the leuco dye (IV), a second semiquinone ion acting as a hydrogen acceptor for the latter step. The leuco dye may then be considered to be oxidized to the dye (V) by another semiquinone ion.

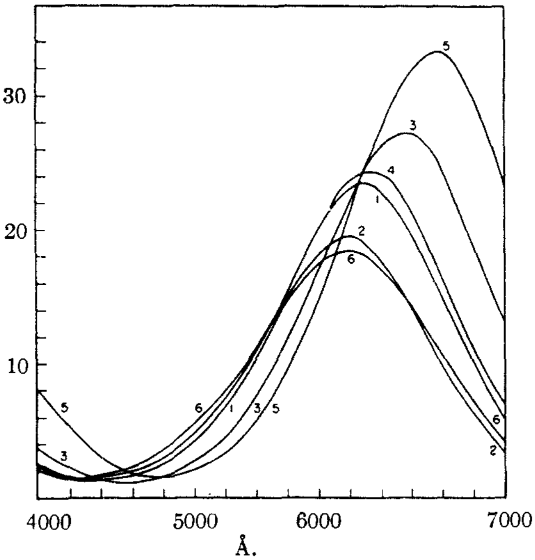
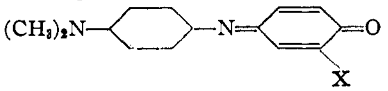
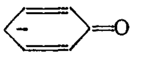


Fig. 1.—Absorption of dyes

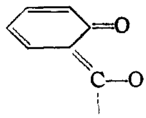


in methanol: (1) X = H; (2) X = CH$_3$; (3) X = Cl; (4) X = -NHCOCH$_3$; (5) X = -CH=CHCOC$_6$H$_5$; (6) X = -OCH$_3$.

The failure of phenols having *o*-CO— or —CH=N— groups to enter the dye-forming reaction may be explained by a reasonable extension of this mechanism, taking into account the resonance systems of the phenolate ions. With phenol itself, structures such as VI, in addition to the Kekulé structures, probably make an appreciable contribution to the state of the ion,[10] and this structure probably contributes largely to the stable activated complex in the dye-forming reaction. When an *o*-CO— group is present, however, structures analogous to VI are probably relatively unimportant compared to structures such as VII,[11] in which the carbon *p*- to the phenolic oxygen is not activated to the extent necessary for the dye-forming reaction.



VI



VII

The absorption spectra of the dyes were determined in four solvents selected to cover a wide range of polarity. Figure 1 shows the absorption curves for some of the dyes in methanol, illustrating their general shape. The values for $\lambda_{\max.}$ and $\epsilon_{\max.}$ are listed in Table II, and some of them are arranged graphically in Figs. 2 and 3.

Interpretation of these absorption data follows that of the parent dye, Phenol Blue (VIII, X=H), which is best represented by the resonance scheme VIIIa $\leftrightarrow$ VIIIb.[12] Brooker and Sprague[13] showed that the absorption of Phenol Blue was affected by the solvent, the absorption band in the visible region moving in the direction of longer wave length as the polarity of the solvent was increased. This behavior was explained on the basis that the inherently unstable dipolar structure VIIIb was made more stable by the more polar solvents. It

---

[8] Thomas and Weissberger, in Mees, "The Theory of the Photographic Process," The Macmillan Co., New York, N. Y., 1942, p. 394.

[9] Michaelis, *Ann. N. Y. Acad. Sci.*, **XL**, Art. 2, 64 (1940). A complete formulation of the resonance system of the semiquinone ion would have to show also the contributions from the possible *p*- and *o*-quinonoid structures.

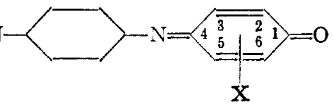
[10] Wheland, "The Theory of Resonance and its Application to Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 168.

[11] A resonance system involving structures such as VII, in addition to the Kekulé structures, may account for the ultraviolet absorption spectrum of salicylaldehyde in alkaline solution; see Morton and Stubbs, *J. Chem. Soc.*, 1347 (1940).

[12] Schwarzenbach and Michaelis, This Journal, **60**, 1667 (1938).

[13] Brooker and Sprague, *ibid.*, **63**, 3214 (1941).

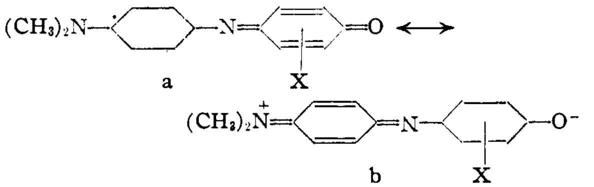
TABLE II

ABSORPTION OF DYES: $(CH_3)_2N$—

Substituent, X	Cyclohexane $\lambda_{max.}$ Å.	Cyclohexane $\epsilon_{max.} \times 10^{-3}$	n-Butyl acetate $\lambda_{max.}$ Å.	n-Butyl acetate $\epsilon_{max.} \times 10^{-3}$	Methanol $\lambda_{max.}$ Å.	Methanol $\epsilon_{max.} \times 10^{-3}$	1:1 Acetone-Water $\lambda_{max.}$ Å.	1:1 Acetone-Water $\epsilon_{max.} \times 10^{-3}$
-H	5520	15.8	5750	19.3	6100	23.5	6340	28.7
2-CH_3	5490	15.5	5710	17.5	6000	19.6	6160	22.7
3-CH_3	5520	13.3	5760	15.7	6070	18.3	6290	20.8
2-Cl	5780	[a]	6020	24.3	6350	27.3	6670	33.3
3-Cl	5780	18.7	6050	22.0	6380	26.2	6750	33.7
2-Br	5790	20.0	6050	24.7	6370	29.2	6720	38.5
2-OCH_3	5450	[a]	5670	15.7	6000	18.5	6200	21.0
3-OCH_3	5430	11.8	5660	14.5	5990	18.0	6200	21.8
2-$NHCOCH_3$	5800	22.3	5970	23.3	6140	24.3	6410	27.8
3-$NHCOCH_3$	5360	[a]	5630	17.3	6010	21.9	6200	26.0
2-CH_2OH	5660	[a]	5770	18.3	6070	21.3	6290	26.7
2-$CH{=}CHCOC_6H_5$	5950	26.7	6220	30.0	6530	33.2	6820	42.7

[a] Solubility too low to permit determination.

was shown that in water solution VIIIa and VIIIb make approximately equal contributions, and even in benzene solution, VIIIb makes an appreciable contribution.



VIII

The effect of substituents in the phenol ring of the Phenol Blue molecule on its absorption may also be explained qualitatively in terms of their effect on the relative stabilities of VIIIa and VIIIb. If the substituent is one which facilitates, through induction or resonance, the diffusion of the negative charge in VIIIb, the oxygen-containing ring of VIIIb will thereby be enabled to accommodate better the negative charge coming from the charge separation in the dipolar structure. These substituents will thus render VIIIb more stable in any given solvent environment, and give rise to stronger absorption at longer wave lengths. Conversely, a substituent which assists the concentration of the negative charge on the oxygen atom in VIIIb would have the opposite effect, making VIIIb less stable and causing weaker absorption at lower $\lambda_{max.}$ values.

This appears to be a satisfactory explanation for the strong bathochromic action of halogen substituents, whose high electronegativity would have an inductive effect in diffusing the negative

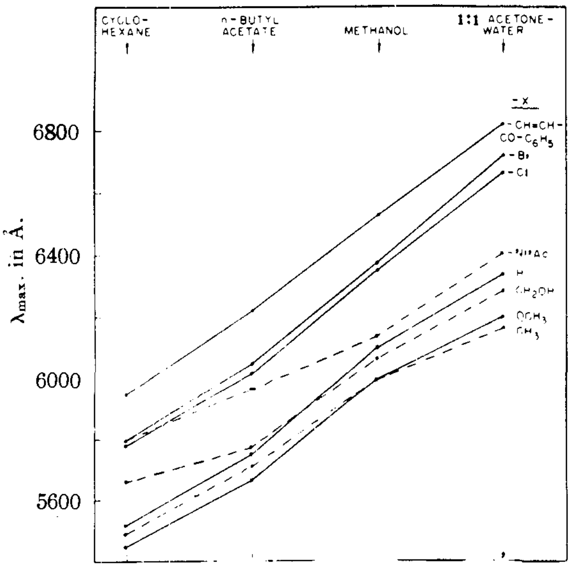
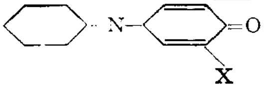


Fig. 2.– $\lambda_{max.}$ of dyes $(CH_3)_2N$  in different solvents.

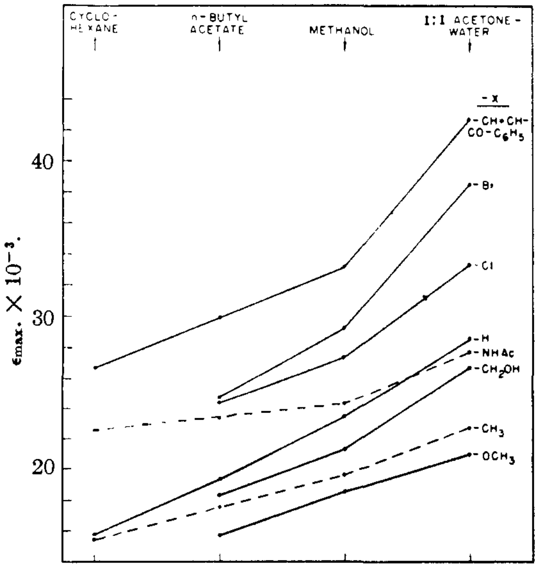
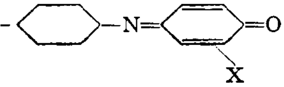
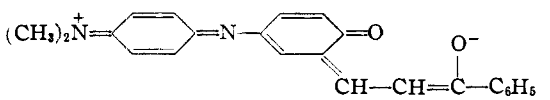


Fig. 3.– $\epsilon_{max.}$ of dyes $(CH_3)_2N$-  in different solvents.

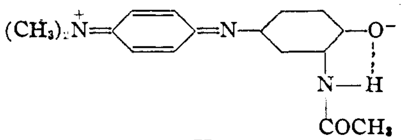
charge in VIIIb. Similarly, the effect of the *o*-$CH{=}CHCOC_6H_5$ group is probably a consequence of its ability to diffuse the negative charge in VIIIb by resonance effects, probably involving contributions from a resonance structure like IX. Compared with Phenol Blue, these substituted dyes show about the same rate of increase of $\lambda_{max.}$ (Fig. 2) with increasing polarity of solvent, but a larger increase in $\epsilon_{max.}$ (Fig. 3) in the more polar solvents. This group of substituents thus appears to permit of a somewhat higher degree of stabilization of the dipolar structure VIIIb by polar solvents.



IX

The small hypsochromic effect of methyl and methoxyl groups may be considered to result from their electropositive nature, which causes an increased concentration of the negative charge on the oxygen in VIIIb. This opposes the separation of charge, rendering VIIIb less stable. Here, the substituted dyes show a smaller increase of $\epsilon_{max.}$ with increasing polarity of solvent than in the case of Phenol Blue, suggesting that these substituents partially interfere with the stabilization of VIIIb by the more polar solvents.

The chloro and methoxyl substituents produce about the same effect when introduced into either the 2- or 3-position. Quite a different result is obtained if the substituent group is acetamino, the introduction of which into the 3-position brings about a lowering of $\lambda_{max.}$ and $\epsilon_{max.}$. This result is explainable in terms of the polarizability of the acetamino group. The 3-acetamino dye shows about the same increase in $\lambda_{max.}$ and $\epsilon_{max.}$ with increasing polarity of solvent as with Phenol Blue itself. An acetamino group in the 2-position, however, causes a strong *increase* in $\lambda_{max.}$ and $\epsilon_{max.}$ in solvents of low polarity and, moreover, these values show a much smaller rate of increase as the polarity of the solvent is increased. This striking behavior indicates an intermolecular stabilization of the resonance structure VIIIb, which could result from a hydrogen bonding, as shown in X. The hydrogen bond in X would be expected to be stronger than an analogous one formed in the other extreme resonance structure, VIIIa (X = $-NHCOCH_3$), because of the larger negative charge in the oxygen in the dipolar structure.[14] The lower rate of increase of $\lambda_{max.}$ and $\epsilon_{max.}$ with increasing polarity of solvent indicates, as might be expected, that the intermolecular stabilization by hydrogen bonding is less effective the more polar the solvent environment.



X

The above considerations of the resonance systems shed some light on the physical stability (to hydrolysis, etc.) of the indoaniline dyes. It seems probable that the stability of these dyes in any given environment should be highest under conditions where the contributions of the two extreme resonance structures VIIIa and VIIIb are most nearly equal, and that any structural change which makes either structure predominate would result in a decrease in the stability of the dye.[15] The instability of the dyes derived from 2,6-dichlorophenol, 2,6-dibromophenol, and *o*-(N-methylacetamino)-phenol may be explained on the basis of this broad generalization. In the first two cases, the two halogen substituents probably greatly increase the contribution of the dipolar structure VIIIb, while in the last case, its contribution is decreased by the $-N(CH_3)COCH_3$ group. Both effects have the end result of reducing the stability of the dye.

Experimental

The organic reactants for preparing the dyes and the solvents used for the spectrophotometric measurements were all Eastman Kodak chemicals, white label grade. Inorganic chemicals of reagent grade were employed.

Preparation of Dyes.—A solution of 37.4 g. (0.22 mole) of silver nitrate in 200 cc. of water was added slowly to a well-stirred solution containing 14.6 g. (0.25 mole) of sodium chloride and 0.3 g. of gelatin[16] in 200 cc. of water. To the suspension of finely divided silver chloride was added, successively, a solution of 20 g. of sodium carbonate monohydrate in 100 cc. of water, and a solution of the phenol (0.025 mole) in 100 cc. of 95% ethanol. Finally, a solution of (0.0275 mole)[17] *p*-aminodimethylaniline hydrochloride in 200 cc. of water was added slowly with vigorous stirring. Dye formation started immediately, and stirring was continued for thirty minutes. Ethyl acetate (or ether) (200 cc.) was then added to the mixture, the whole was stirred well, then filtered to remove silver and residual silver chloride, and the residue washed with small portions of the solvent to remove adhered dye. The ethyl acetate layer containing the dye was separated from the filtrate, washed with water until the wash water was nearly colorless (four or five washes), dried over anhydrous potassium carbonate, and finally evaporated to leave the solid dye. The crude dyes were obtained in 90–98% yields, all of them in a fairly high state of purity so that one or two crystallizations from a suitable solvent yielded products giving correct analyses.

Spectrophotometric Measurements.—All of the spectrophotometric measurements were made on 5.0×10^{-5} *M* solutions in 1-cm. cells, using the General Electric Automatic Recording Spectrophotometer. The authors are grateful to Mr. E. E. Richardson for making the spectrophotometric measurements.

Summary

Indoaniline dyes have been prepared from *p*-aminodimethylaniline and a group of simple

---

[14] Pauling, "Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, New York, 1940, p. 307.

[15] It is planned to treat in more detail in a later paper of this series some of the factors affecting the stability of indoaniline and related dyes.

[16] The gelatin (either photographic or edible grade) was dissolved separately in 10–20 cc. of water by soaking at room temperature for several hours, then warming to 50° to dissolve.

[17] It is essential that a slight molar excess of the *p*-phenylenediamine be used, since any unreacted phenol was found to be very difficult to separate from the dye.

phenols, using an improved procedure employing silver chloride as the oxidizing agent.

The absorptions of the dyes have been determined in four solvents covering a wide range of polarity. The effects of the various substituents on the absorption are explained qualitatively in terms of their effects on the resonance systems involved.

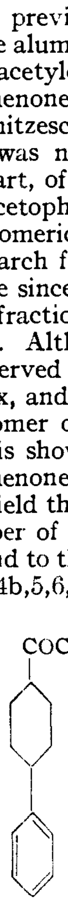
Rochester, New York Received July 8, 1946

[Contribution from the Laboratory of Organic Chemistry of the University of Wisconsin]

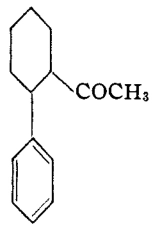
Some Observations on Friedel–Crafts Reactions Involving Unsaturated Ketones. 9-Keto-4b,5,6,7,8,8a,9,10-octahydrophenanthrene

By C. David Gutsche and William S. Johnson

In a previous communication[1] it was shown that the aluminum chloride-catalyzed reaction between acetylcyclohexene (or 2-chlorohexahydroacetophenone) and benzene, which was discovered by Nenitzescu and Gavat,[2] afforded a product which was not homogeneous, but consisted, in large part, of a crystalline form of 4-phenylhexahydroacetophenone, I. The presence of another stereoisomeric form of I was also demonstrated. In a search for other substances in the mixture, we have since submitted the crude reaction product to fractional distillation through an efficient column. Although this work is as yet incomplete it has served to indicate that the mixture is very complex, and has made possible the isolation of a new isomer of I, melting at 80–81°. This substance is shown below to be 2-phenylhexahydroacetophenone, II, and although isolated only in small yield the discovery of its presence has led to a number of interesting experiments and conclusions and to the synthesis of the hitherto unknown 9-keto-4b,5,6,7,8,8a,9,10-octahydrophenanthrene, IX.

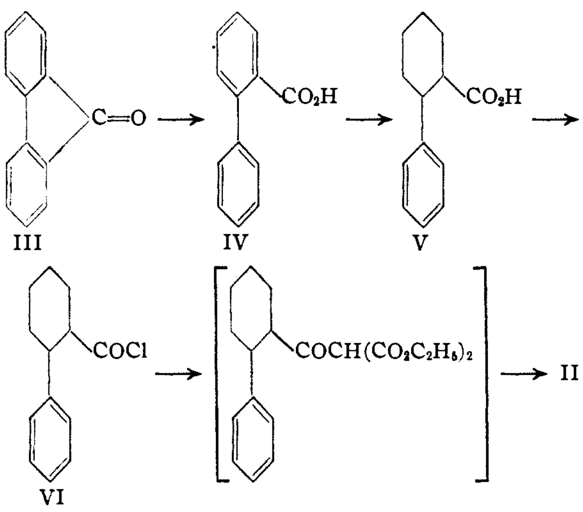


I



II

To prove the identity of the 81° ketone with the previously known 2-phenylhexahydroacetophenone reported to melt at 78–79°,[3] the latter was synthesized for comparison. The method of Kipping and Perkin[3] which involves the condensation of 1-phenyl-1,5-dibromopentane with acetoacetic ester appeared unpromising because of the inaccessibility of starting materials and the poor yields. A new synthesis was therefore developed involving the sequence of reactions indicated in the accompanying flow sheet.



The cleavage of fluorenone, III, with potassium hydroxide by the excellent procedure of Huntress and Seikel[4] gave 2-phenylbenzoic acid, IV, in 93–96% yields. Reduction of IV with sodium and amyl alcohol afforded the previously known[3] stereoisomer of 2-phenylcyclohexanecarboxylic acid, V, in 73% yield. The acid chloride VI was prepared and treated with sodiomalonic ester followed by acid hydrolysis without isolation of the intermediate keto di-ester. The over-all yield of II from V was 84%. The ketone thus obtained proved to be identical with that isolated from the Friedel–Crafts reaction as confirmed by mixed melting point determinations with the ketones and 2,4-dinitrophenylhydrazones.

Cook and Hewett[5] have made attempts to cyclize phenylacetylcyclohexene, VIII, to the keto-octahydrophenanthrene IX, using aluminum chloride or sulfuric acid, but they were able to isolate only recovered starting material. This failure to effect ring closure has since been confirmed by Bergs and Wittfeld,[6] and is indeed surprising in view of the fact that such a cyclization would represent the intramolecular counterpart of the Friedel–Crafts reaction to produce II described above. We have, therefore, reinvestigated this work.

---

[1] Johnson and Offenhauer, This Journal, **67**, 1045 (1945).

[2] Nenitzescu and Gavat, *Ann.*, **519**, 260 (1935).

[3] Kipping and Perkin, *J. Chem. Soc.*, 304 (1890).

[4] Huntress and Seikel, This Journal, **61**, 816, 1066, 1358 (1939).

[5] Cook and Hewett, *J. Chem. Soc.*, 1098 (1933).

[6] Bergs and Wittfeld, *Ber.*, **67**, 238 (1934).