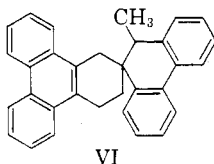


$m\mu$ with ϵ ($\times 10^4$) 6.35, 3.32, and 1.44 respectively. Low intensity absorption at 343 and 362 $m\mu$ has ϵ 1.92×10^3 . This spectrum is almost identical with that of the dihydro dimer of 9,10-phenanthraquinodimethane (VI).⁴ Extinction coefficients of low intensity absorption make it clear that only one of the phenanthrene nuclei retains the 9,10-double bond. On the basis of these data, and in consistency with characterized quinone methide dimers in other series,⁵ the substance is formulated as V.



EXPERIMENTAL⁶

9-Phenanthrol. This substance was prepared by the procedure of Bachman⁷ (22–40% yields) and also by application of the method developed by Hawthorne⁸ for another phenol (26% yield).

10-Dimethylaminomethyl-9-phenanthrol (IV) and its methiodide. A solution of 5.9 g. of 9-phenanthrol in 20 ml. of ethanol was treated with 6.0 ml. of 25% aqueous dimethylamine and 2.3 ml. of 36% aqueous formaldehyde. After standing for 8 hr. at room temperature, the mixture was freed of solvent, without heating, at an aspirator. The solid residue (crude IV) could not be purified without decomposition and so was dissolved in ether and converted to the methiodide using 5.0 g. of methyl iodide. After 12 hr. at room temperature the salt was collected by filtration and washed with ether. The methiodide in this crude state (4.0 g. 35%) melted with decomposition at 225°. Attempts to purify it resulted in the formation of V.

Anal. Calcd. for $C_{18}H_{20}NI$: N, 3.55. Found: N, 3.92.

Dimer of 10-methylene-9-phenanthrone (V). A solution of 7.0 g. of 9-phenanthrol, 3.2 ml. of 38% aqueous formaldehyde and 6.2 ml. of 25% aqueous dimethylamine in 60 ml. of ethanol was heated under reflux for 2 hr. The mixture, containing suspended yellow solid, was filtered and the filtrate was concentrated to a small volume whereupon additional solid crystallized. The combined solids were recrystallized from benzene to give 3.2 g. (43%) of well formed yellow prisms of V, m.p. 251–252°.

Anal. Calcd. for $C_{30}H_{20}O_2$: C, 87.35; H, 4.89. Found: C, 87.13; H, 4.82.

Spectral data are described in the discussion section.

A similar experiment in which the dimethylamine was replaced by a catalytic quantity of pyridine gave the same substance in 40% yield. Reactions conducted in the absence of base of any kind afforded the dimer in 36% yield.

Lithium aluminum hydride reduction of V. One gram of the dimer (V) was heated for 10 hr. under reflux in a suspension of a very large excess of lithium aluminum hydride in 50 ml. of tetrahydrofuran. Excess hydride was destroyed by

(3) C. A. Coulson, D. P. Craig, A. Maccoll, and A. Pullman, *Discussions Faraday Soc.*, **2**, 46 (1947).

(4) P. D. Gardner and H. Sarrafzadeh R., *J. Am. Chem. Soc.*, in press.

(5) See for example K. Hultsch, *J. prakt. Chem.*, **159**, 180 (1941).

(6) Melting points are corrected. Infrared spectra were obtained in potassium bromide wafers. Ultraviolet spectra were of 95% ethanol solutions.

(7) W. E. Bachman, *J. Am. Chem. Soc.*, **56**, 1363 (1934).

(8) M. F. Hawthorne, *J. Org. Chem.*, **22**, 1001 (1957).

the cautious addition of water followed by dilute hydrochloric acid. Isolation of the product by ether extraction and the usual processing of the extract afforded 0.90 g. (90%) of the expected carbinol, m.p. 249–250°. This substance appeared as colorless prisms after several recrystallizations from ethyl acetate and had the same melting point. The carbonyl absorption found at 5.94 μ in V was lacking in the spectrum of the carbinol. Hydroxyl absorption appeared at 2.9 μ . The ultraviolet spectrum is described in the discussion.

Anal. Calcd. for $C_{30}H_{22}O_2$: C, 86.93; H, 5.35; mol. wt. 414. Found: C, 86.64; H, 5.15; mol. wt. 480 (cryoscopic in benzol).

Acknowledgment. The authors are indebted to the Robert A. Welch Foundation for the financial support of this work.

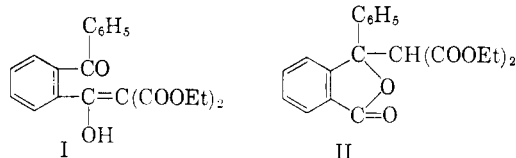
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Condensation of *o*-Benzoylbenzoyl Chloride with Ethyl Malonate

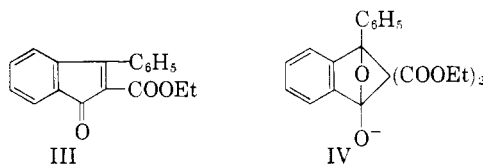
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The compound formed by action of *o*-benzoylbenzoyl chloride on ethoxymagnesiummalonic ester, formerly represented as ethyl 3-phenylphthalidylmalonate (II),¹ is actually the enol form of ethyl *o*-benzoylbenzoylmalonate (I).



Structure I allows simple formulation of the conversion of the substance into ethyl 3-phenylindone-2-carboxylate (III) by aqueous base, whereas with structure II this change requires assumption of a strained intermediate (IV).

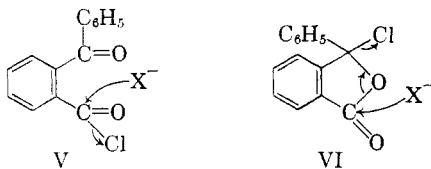


Spectral and chemical properties of the compound are in agreement with I. In chloroform the compound has a sharp absorption band at 3500 cm^{-1} (enolic OH), a broad band with maxima at 1600, 1650, 1725 and 1770 cm^{-1} (C=O and C=C—O), and a broad band at 1260–1300 cm^{-1} (ester). It gives a deep red-brown color with ferric chloride, and it is soluble in cold 1% sodium hydroxide. Acidification of this solution, if it has not been


(1) W. L. Yost and A. Burger, *J. Org. Chem.*, **15**, 1113 (1950).

heated or kept too long, precipitates the compound unchanged.

Formation of I has no bearing on the true structure of *o*-benzoylbenzoyl chloride, as illustrated by V and VI.



Authentic ethyl 3-phenylphthalidylmalonate (II) can be obtained in good yield from ethyl *o*-benzoylbenzoate and ethyl sodiomalonate in alcohol. The properties of this substance are quite different from those of its isomer. Its infrared spectrum shows absorption at 1720 and 1770 cm^{-1} , corresponding to lactone and ester carbonyl groups. It gives no ferric chloride color and it is insoluble in cold dilute sodium hydroxide. When it is heated with the latter reagent, it dissolves, and acidification then precipitates 3-phenylphthalidyl malonic acid. Heating this acid yields the known² 3-phenylphthalidylacetic acid, also obtained directly from the malonic ester by acid hydrolysis.

By analogy with the present results, it is probable that the compound obtained from ethyl benzoylbenzoate and benzyl cyanide is not $\text{C}_6\text{H}_5\text{COC}_6\text{H}_4\text{-COCHCN}$,³ but rather $\text{HOOC}_6\text{H}_4\text{C}=\text{CCN}$ or  the corresponding lactone. The reported stability to hydrolysis then is easily understandable, and the methylation product is a methyl ester.

EXPERIMENTAL

Ethyl o-benzoylbenzoylmalonate (I). Slight modification of the original preparation¹ enables one to obtain yields of 90–95%. It was not necessary to avoid heating benzoylbenzoyl chloride, and the material was freed of thionyl chloride at 100° under reduced pressure, two portions of dry benzene being added to insure complete volatilization. As I is soluble in and rapidly altered by aqueous sodium carbonate, an excess must be avoided in final washing of the crude product; furthermore, the compound is quite soluble in ether and it is well to use 2:1 ether-ligroin (30–60°) for the first crystallization. The crude product obtained in the present research melted at 80–85°; recrystallization from ethyl acetate-ligroin gave clear prisms, m.p. 86–88° (lit.,¹ 77–79°).

Anal. Calcd. for $\text{C}_{21}\text{H}_{20}\text{O}_6$: C, 68.5; H, 5.5. Found: C, 68.4; H, 5.4.

Ethyl 3-phenylphthalidylmalonate (II). A solution of 10 g. of sodium in 100 ml. of absolute alcohol was treated with 70 g. of ethyl malonate and then 100 g. of ethyl benzoylbenzoate. The mixture was boiled for 1.5 hr. and then distilled to a sirup under reduced pressure. Addition of 400 ml. of

water gave a cloudy solution from which ether extraction (2×100 ml.) removed 9.1 g. of ethyl malonate and 20 g. of ethyl benzoylbenzoate. The product was precipitated by acidification as an oil which soon solidified; recrystallization from alcohol and then from ethyl acetate-ligroin gave 95 g. of colorless needles m.p. 100–102°.

Anal. Calcd. for $\text{C}_{21}\text{H}_{20}\text{O}_6$: C, 68.5; H, 5.5. Found: C, 68.5; H, 5.6.

When II was boiled with 10% sodium carbonate for about 5 min., it gave a colorless solution. Acidification gave an oil which solidified when it was dried and rubbed with ether. Crystallization from ethyl acetate-ligroin gave an *acid-ester*, colorless needles, m.p. 97–98° that frothed at about 145°.

Anal. Calcd. for $\text{C}_{19}\text{H}_{16}\text{O}_6$: C, 67.0; H, 4.7. Found: C, 66.7; H, 4.5.

When 1 g. of II was boiled for 1 hr. with 4 ml. of acetic acid and 4 ml. of 48% hydrobromic acid, it gave 3-phenylphthalide-3-acetic acid, needles from toluene, m.p. 177–178° with previous sintering (lit.,² m.p. 179–181°); boiling the acid with methanol-sulfuric acid gave *methyl 3*-phenylphthalid-3-acetate, needles from methanol, m.p. 86–87°; b.p. 230–232° at 10 mm.

Anal. Calcd. for $\text{C}_{17}\text{H}_{14}\text{O}_4$: C, 72.3; H, 5.0. Found: C, 72.0; H, 5.0.

When 6.7 g. of II was boiled 15 min. with 4 g. of sodium hydroxide in 25 ml. of water and the resulting solution was then cooled and acidified, there was obtained 5.3 g. crude *3*-phenylphthalidylmalonic acid, a white powder nearly insoluble in hot acetic acid, ethyl acetate, benzene, or chloroform. Acetone dissolved it easily, however, and crystallization from acetone-ligroin gave 4.1 g. of colorless needles, m.p. 160–164° with gas evolution; the melt resolidified and then melted again at 176–178°.

Anal. Calcd. for $\text{C}_{17}\text{H}_{12}\text{O}_6$: C, 65.4; H, 3.9. Found: C, 65.2; H, 3.9.

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Condensation Reactions of Phthalaldehydic Acid. I

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On the basis of certain reactions of phthalaldehydic acid several early investigators^{1,2} postulated a tautomeric closed-ring form for this compound. This view is substantiated in a recent paper by Wheeler, Young, and Erley,³ who have examined the infrared absorption of phthalaldehydic acid. These investigators also give data for a considerable number of substituted phthalides prepared by syntheses involving the very reactive 3-position in the 3-hydroxyphthalide form. However, in none of the phthalides which they describe is the carbon atom at the 3-position linked directly to carbon in the substituent.

The solubility and stability of phthalaldehydic

(2) W. S. Johnson, A. L. McCloskey, and D. A. Dunigan, *J. Am. Chem. Soc.*, **72**, 514 (1950).

(3) W. Wislicenus, H. Eichert, and M. Marquardt, *Ann.*, **436**, 95 (1923).

(4) The author thanks Mrs. O. Hamerston for analytical work.

(1) S. Racine, *Ber.*, **19**, 778 (1886).

(2) Bistrzycki and Yessel de Schepper, *Ber.*, **31**, 2790 (1898).

(3) D. D. Wheeler, D. C. Young, and D. S. Erley, *J. Org. Chem.*, **22**, 556 (1957).