

TABLE I

Polymer from	Approx. mol. wt.	Softening point, °C.	Nitromethane	Solubility		Empirical formula	Analyses, %					
				Chloroform	Benzene		Calcd.		Found		N	
<i>p</i> -Cyanostyrene <sup>a</sup>	5310	200-225	+	-	-	C <sub>9</sub> H <sub>7</sub> N	83.72	5.42	10.85	81.86	5.49	10.46
<i>p</i> -Vinylbenzoic acid <sup>b</sup>	4710	165-200	+	+	-	C <sub>9</sub> H <sub>8</sub> O <sub>2</sub>	72.97	5.40		68.85	5.17	
Methyl <i>p</i> -vinylbenzoate	45000	205-212	+	+	+	C <sub>10</sub> H <sub>10</sub> O <sub>2</sub>	74.07	6.17		71.96	5.72	

<sup>a</sup> Also soluble in dimethylformamide. <sup>b</sup> Also soluble in 5 per cent. sodium hydroxide solution.

The polymer of *p*-cyanostyrene was prepared in a similar manner. It was purified by dissolving in 30 cc. of nitromethane and reprecipitated by slowly dropping this solution into 250 cc. of methanol. This process of purification was repeated and the powder obtained was dried for several days. This polymer was insoluble in benzene and chloroform but did dissolve in dimethylformamide as well as nitromethane.

The polymer of *p*-vinylbenzoic acid was obtained in the purification of the monomer. Upon successive recrystallization of *p*-vinylbenzoic acid from an aqueous ethanol solution, without an inhibitor present, the polymer precipitated from solution upon gentle refluxing for several hours. This polymer was removed by filtration and dried in a vacuum desiccator for several weeks. It was only slightly soluble in benzene but completely soluble in chloroform and nitromethane.

The analyses and physical properties of these three polymers are described in the table.

The analytical figures indicate that these substituted styrene polymers like the polymer of styrene itself take up a considerable amount of oxygen as a part of the molecule during polymerization.<sup>10</sup>

### Summary

*p*-Cyanostyrene, *p*-vinylbenzoic acid and methyl *p*-vinylbenzoate have been synthesized and the corresponding vinyl polymers briefly characterized.

(10) Price and Tate, *THIS JOURNAL*, **65**, 517 (1943).

URBANA, ILLINOIS

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF PARKE, DAVIS AND COMPANY]

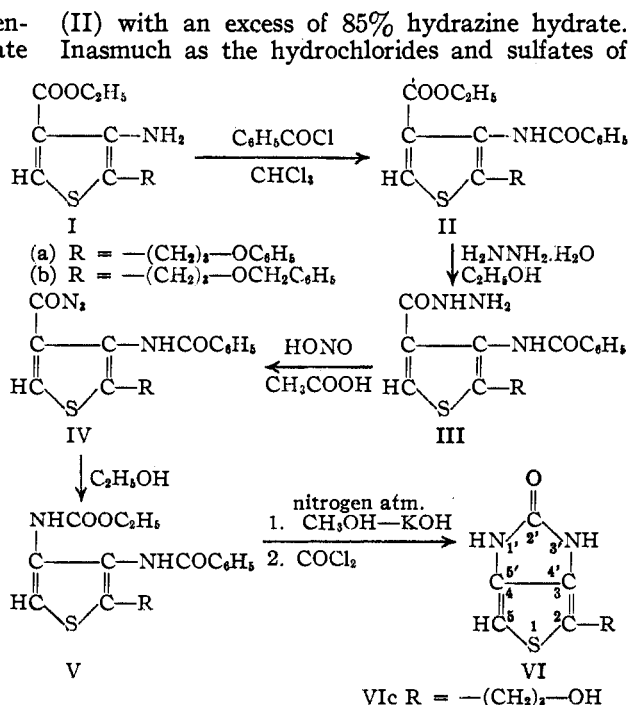
## Derivatives of 2'-Keto-3,4-imidazolidothiophene

BY LEE C. CHENEY AND J. ROBERT PIENING

The aromatization of ethyl 3-keto-2- $\gamma$ -phenoxypropyl-4-tetrahydrothiophenecarboxylate (II) with an excess of 85% hydrazine hydrate. Inasmuch as the hydrochlorides and sulfates of the hitherto unknown ethyl 3-amino-2- $\gamma$ -phenoxypropyl-4-thiophenecarboxylate (Ia). Because the readily accessible parent keto ester had been prepared by an unambiguous ring closure,<sup>2</sup> the structure of Ia could be assigned without reservation, thus rendering the compound particularly well suited as a model in experiments aimed toward the ultimate synthesis of 2,3,4,5-tetrahydrobiotin.<sup>3</sup>

By means of the sequence of reactions featuring the Curtius degradation as pictured on the flow sheet, an unequivocal synthesis of 2'-keto-3,4-imidazolido-2- $\gamma$ -phenoxypropylthiophene (VIa) was achieved. The corresponding benzyl ether (VIb) was then prepared from Ib by an extension of the same general method.

The amino esters (I) were first benzoylated by a modification of the method of Jacobs and Heidelberg.<sup>4</sup> However, the more convenient procedure of refluxing a chloroform solution of the weakly basic amines with an excess of benzoyl chloride was found to give satisfactory results. The hydrazides (III) were obtained in yields of 88-95% by boiling an alcoholic solution of the acylated amino esters



the hydrazides (III) were practically insoluble in water, the conventional procedure for carrying out the Curtius degradation<sup>5</sup> was considered inappro-

(1) Cheney and Piening, *THIS JOURNAL*, **67**, 729 (1945).

(2) Cheney and Piening, *ibid.*, **67**, 2213 (1945).

(3) Cheney and Piening, *ibid.*, **66**, 1040 (1944); **67**, 731 (1945).

(4) Jacobs and Heidelberg, *ibid.*, **39**, 1439 (1917).

(5) Pertinent examples are the following: Windaus and Dalmer, *Ber.*, **53**, 2304 (1920); Robinson and Todd, *J. Chem. Soc.*, 1743 (1939).

appropriate. Consequently the acid azides were prepared in acetic acid.<sup>8</sup> Decomposition of the azides (IV) by heating in an inert solvent such as xylene or toluene produced the corresponding isocyanates in practically quantitative yields. In view of the reported cyclization of 2-carbomethoxyaminobenzoic acid azide to 1-carbomethoxyamino-2(3)-benzimidazolone under comparable conditions,<sup>7</sup> the ring closure of IV to form VI benzoylated in the 3'-position was considered a possibility, but no trace of such a reaction product could be isolated. Moreover, heating the isocyanate derived from IVa under nitrogen to a temperature of 230° caused some decomposition but failed to induce cyclization. By refluxing the acid azides (IV) with a large excess of absolute alcohol the urethans (V) were produced in excellent yields. In like manner, the identical urethans were obtained from the isocyanates, thus proving the structure of the latter.

Owing to the extreme sensitivity of the free 3,4-diaminothiophene derivatives to atmospheric oxygen, the conversion of V into VI in satisfactory yields required the application of an inert atmosphere throughout the continuous operations of the alkaline hydrolysis and the treatment with phosgene. Although these water-insoluble imidazolidothiophene derivatives are pictured in the keto form (VI), their solubilities in dilute solutions of sodium and potassium hydroxide indicate the existence of a tautomeric system analogous to that exhibited by 2(3)-benzimidazolone.<sup>8</sup>

Inasmuch as VI were found to resinify when heated with strong mineral acids of a higher concentration than one normal, possible ways of effecting ether cleavage to obtain 2'-keto-3,4-imidazolido-2- $\gamma$ -hydroxypropylthiophene (VIc) or the corresponding halides were indeed limited. Nevertheless, several methods for ether scission, including the use of alkali dissolved in a glycol,<sup>9</sup> pyridine hydrochloride<sup>10</sup> and boron bromide,<sup>11</sup> were applied to the phenyl ether (VIa). Although phenol was generally identified as a reaction product, the desired alcohol or halide could not be isolated in any case. Attention was then focused on the more vulnerable<sup>12</sup> benzyl ether (VIb). The poisoning effect of the sulfur in the molecule precluded catalytic debenzoylation<sup>13</sup> with palladium catalysts. Finally, excellent results were obtained by the use of sodium in liquid ammonia by the method of Patterson and du Vigneaud<sup>14</sup> applied to the scission of benzylthio ethers. The close correspondence of the ultraviolet absorption

(6) Buning, *Rec. trav. chim.*, **40**, 327 (1921).

(7) Lindemann and Schultheis, *Ann.*, **464**, 237 (1933).

(8) Heller, Buchwaldt, Fuchs, Kleinicke and Kloss, *J. prakt. Chem.*, **111**, 1 (1925).

(9) Corse, U. S. Patent 2,325,307 (1943).

(10) Prey, *Ber.*, **75**, 350, 537 (1942).

(11) Benton and Dillon, *THIS JOURNAL*, **64**, 1128 (1942).

(12) Tronow and Ladigina, *Ber.*, **62**, 2844 (1929); Schorigin, *ibid.*, **56**, 176 (1923); **57**, 1627 (1924).

(13) Baltzy and Buck, *THIS JOURNAL*, **65**, 1984 (1943).

(14) Patterson and du Vigneaud, *J. Biol. Chem.*, **111**, 393 (1935); Miller and du Vigneaud, *ibid.*, **108**, 753 (1935).

curve for VIc to that for VIb<sup>8</sup> shows that no other structural alterations accompany the ether cleavage.

Attempts to extend the side-chain of VIc to a valeric acid *via* the chloride or bromide through the malonic ester synthesis proved unsuccessful owing to unfavorable concurrent reactions encountered in the preparation of the halide.

Compounds VIa, VIb and VIc have been tested by microbiological methods for biotin and antibiotin activity. In biotin assays using *L. arabinosus* and *S. cerevisiae*, no activity was found to a concentration of 800  $\gamma$  per 10 ml. of medium whereas biotin itself is active at a range of 0.1 to 1.0 m $\gamma$  per 10 ml. of medium. The same concentration failed to reverse the activity of a minimal amount of biotin for growth of *L. arabinosus*.

### Experimental<sup>15</sup>

**Ethyl 3-Benzamido-2- $\gamma$ -phenoxypropyl-4-thiophenecarboxylate (IIa).**—(a) To a warm solution of 14.1 g. (0.046 mole) of ethyl 3-amino-2- $\gamma$ -phenoxypropyl-4-thiophenecarboxylate (Ia) in 100 ml. of glacial acetic acid was added 100 ml. of a saturated solution of sodium acetate. The well-stirred suspension was cooled in an ice-bath and 8 ml. (0.069 mole) of benzoyl chloride was added dropwise. Lumps of solid soon separated. After being stirred for forty minutes, the suspension was filtered and washed with ice water. The granular product was dissolved in 180 ml. of hot glacial acetic acid, treated with 70 ml. of a saturated solution of sodium acetate, cooled in ice and again treated with 8 ml. of benzoyl chloride. As soon as the suspension solidified, the ice-bath was removed, 50 ml. of water was added and the mixture was stirred at room temperature for three and one-half hours. Then 100 ml. of water was added and the suspension was cooled, filtered, washed with cold water and dried. After crystallization from alcohol the product, m. p. 97–98°, weighed 15.7 g. (83% yield); A sample of the compound was recrystallized from alcohol to obtain colorless needles, m. p. 98–99°.

*Anal.* Calcd. for C<sub>21</sub>H<sub>21</sub>O<sub>4</sub>NS: C, 67.45; H, 5.66. Found: C, 67.38; H, 5.91.

(b) A solution of 29.2 g. (0.096 mole) of the amino ester Ia in 100 ml. of dry chloroform was treated with 12.6 ml. (0.109 mole) of benzoyl chloride. The dark solution was then refluxed for twenty-one hours. Chloroform was removed by steam distillation. After chilling the flask the water was decanted and the residue was crystallized from alcohol. Recrystallization from alcohol gave 31.1 g. (79.5% yield) of product, m. p. 95–96.5°, pure enough to give satisfactory results in the next step.

**3-Benzamido-2- $\gamma$ -phenoxypropyl-4-thiophenecarboxylic Acid Hydrazide (IIIa).**—A mixture of 14.6 g. (0.0357 mole) of the aforementioned ester (IIa), 100 ml. of absolute alcohol and 25 ml. of hydrazine hydrate (85%) was refluxed for sixteen hours, during which time white crystals separated from solution. After removal of excess hydrazine by distillation under reduced pressure the crystalline mass was boiled with 700 ml. of absolute alcohol, cooled and the crystals were collected. Following desiccation the lustrous needles melted at 186.5–187.5°; yield 13.1 g. (93%). Recrystallization from alcohol did not alter the melting point.

*Anal.* Calcd. for C<sub>21</sub>H<sub>21</sub>O<sub>4</sub>N<sub>2</sub>S: C, 63.77; H, 5.35. Found: C, 63.77; H, 5.29.

For proof of the hydrazide structure, 0.1 g. of the compound was dissolved in 20 ml. of absolute alcohol, treated with 0.2 ml. of anisaldehyde and refluxed for ten hours. Dilution with water precipitated a product which melted at 175.5–176.5°. Recrystallization from alcohol gave the **anisalhydrazide** as fine, white needles, m. p. 176.5–177°.

(15) All melting points are corrected.

*Anal.* Calcd. for  $C_{25}H_{27}O_4N_3S$ : C, 67.81; H, 5.30. Found: C, 68.17; H, 5.39.

**3-Benzamido-2- $\gamma$ -phenoxypropyl-4-thiophenecarboxylic Acid Azide (IVa).**—After dissolving 7.91 g. (0.020 mole) of the corresponding hydrazide (IIIa) in 200 ml. of glacial acetic acid by the application of heat, the well-stirred solution was cooled in an ice-bath and treated with 2.25 ml. of concentrated hydrochloric acid. A fine white precipitate of the hydrazide hydrochloride formed immediately. Then a solution of 1.50 g. (0.022 mole) of sodium nitrite in 35 ml. of water was added dropwise during seven minutes and the reaction mixture was stirred in the ice-bath for an additional two hours. Following filtration the white microcrystalline azide was washed with 100 ml. of ice water and desiccated *in vacuo* over phosphorus pentoxide; yield 7.4 g. (91%); decomposition point 108–109°.

*Anal.* Calcd. for  $C_{21}H_{18}O_3N_4S$ : C, 62.05; H, 4.46; N, 13.79. Found: C, 62.30; H, 4.24; N, 13.78.

**3-Benzamido-2- $\gamma$ -phenoxypropyl-4-thienyl Isocyanate.**—A solution of 2.0 g. (0.0049 mole) of the aforementioned azide (IVa) in 50 ml. of sodium-dried xylene was refluxed in a wax-bath at 170–180° for eight hours. The xylene was distilled under reduced pressure, leaving small crystals which were rinsed into a Büchner funnel with 35 ml. of dry petroleum ether; weight 1.86 g. (quantitative yield); m. p. 191.5–193°. Recrystallization of the product from toluene raised the melting point to 194.5–195°.

*Anal.* Calcd. for  $C_{21}H_{18}O_3N_2S$ : N, 7.40. Found: N, 7.33.

**3-Benzamido-4-carbomethoxyamino-2- $\gamma$ -phenoxypropylthiophene (Va).**—(a) One gram (0.00246 mole) of the azide IVa was refluxed with 100 ml. of absolute alcohol for five hours while a calcium chloride tube excluded moisture. The solution was then concentrated to a volume of about 45 ml. and hot water was added to make the total volume 125 ml. Cooling in an ice-salt-bath, filtration and desiccation produced 1.04 g. (quantitative yield) of the urethan, m. p. 144–145°. Recrystallization of a sample from alcohol gave silky needles, m. p. 146–146.5°.

*Anal.* Calcd. for  $C_{23}H_{24}O_4N_2S$ : C, 65.07; H, 5.70. Found: C, 65.31; H, 5.81.

(b) One gram (0.00264 mole) of 3-benzoylamino-2- $\gamma$ -phenoxypropyl-4-thienyl isocyanate was suspended in 100 ml. of absolute alcohol and refluxed for five hours while protected from moisture. Concentration of the alcoholic solution followed by cooling led to the crystallization of 0.88 g. (79% yield) of colorless needles, m. p. 145–146°, which did not depress the melting point of the urethan obtained directly from the azide by procedure (a).

**2'-Keto-3,4-imidazolido-2- $\gamma$ -phenoxypropylthiophene (VIa).**—Under an atmosphere of purified nitrogen a mixture of 3.05 g. (0.0072 mole) of the aforementioned urethan (Va), 38 g. of potassium hydroxide and 105 ml. of methanol was refluxed on the steam-bath for twenty-two hours. The methanol was distilled under reduced pressure through the upright bulb condenser. The pale pink residue was cooled in an ice-salt-bath and the atmosphere of nitrogen was reestablished. Following the addition of 150 ml. of freshly boiled water cooled to 5° and 200 ml. of ether, phosgene was then slowly bubbled through the cooled, well shaken mixture until the medium was acid to litmus. The aqueous layer was extracted with 600 ml. of ether in four portions. Combined ether extracts were washed with saturated sodium bicarbonate solution. Distillation of solvent left a brown oil which was dissolved in a minimum of boiling 5% potassium hydroxide solution. The brown solution was treated with Darco, filtered and saturated with carbon dioxide to obtain 1.75 g. of light-brown powder, m. p. 171–173°. The addition of warm water to an alcoholic solution of the product yielded 1.62 g. (82%) of tan microcrystals, m. p. 172.5–173.5°. Crystallization from alcohol produced pale-yellow crystals, m. p. 174–174.5°.

*Anal.* Calcd. for  $C_{14}H_{14}O_2N_2S$ : C, 61.29; H, 5.14. Found: C, 61.40; H, 5.09.

**Ethyl 3-Benzamido-2- $\gamma$ -benzyloxypropyl-4-thiophenecarboxylate (IIb).**—A mixture of 2.79 g. (0.00875 mole) of

ethyl 3-amino-2- $\gamma$ -benzyloxypropyl-4-thiophenecarboxylate, 13 ml. of dry chloroform and 1.2 ml. (0.01 mole) of benzoyl chloride was refluxed on the steam-bath for seventeen hours. Chloroform was removed by steam distillation. The oil and water were separated by decantation after cooling and the oil dissolved in alcohol and treated with Darco. The alcohol solution was concentrated and treated with hot water until a faint turbidity remained. An oil separated on cooling so more water was added and the mixture cooled and scratched until the product crystallized. The crude material was collected and dried; yield, 3.4 g. (92%); m. p. ca. 60°. A sample recrystallized thrice from 80% alcohol melted at 65–66°.

*Anal.* Calcd. for  $C_{24}H_{26}O_4NS$ : N, 3.31. Found: N, 3.44.

**3-Benzamido-2- $\gamma$ -benzyloxypropyl-4-thiophenecarboxylic Acid Hydrazide (IIIb).**—A mixture of 2.96 g. (0.007 mole) of the ester (IIb), 20 ml. of absolute alcohol and 5 ml. of 85% hydrazine hydrate was refluxed on the steam-bath for sixteen hours. The solution was cooled for several hours and the flocculent mass of crystals collected and dried, m. p. 116–117°. This fraction weighed 0.64 g. The filtrate was warmed and diluted with three volumes of water. Cooling and stirring produced 1.89 g. more of crude hydrazide, m. p. 110–117°; yield, 2.53 g. (88.5%). A sample recrystallized from alcohol melted at 116–117°.

*Anal.* Calcd. for  $C_{22}H_{22}O_3N_3S$ : N, 10.26. Found: N, 10.07.

**3-Benzamido-2- $\gamma$ -benzyloxypropyl-4-thiophenecarboxylic Acid Azide (IVb).**—A solution of 2.43 g. (0.00594 mole) of the hydrazide (IIIb) in 25 ml. of glacial acetic acid was cooled to 17° and 0.67 ml. of concentrated hydrochloric acid added. To the vigorously stirred solution was slowly added a cold solution of 0.446 g. (0.00646 mole) of sodium nitrite in 10.5 ml. of water. After half an hour water was added dropwise until the solution was turbid. An oil formed soon after but addition of more water caused crystallization to begin. The mixture was stirred another half an hour before filtering off the crystals. The white product was washed thoroughly with ice water and dried in a vacuum desiccator. The yield of crude azide was 2.34 g. (93.5%); m. p. 62–64° with gas evolution. This compound was not analyzed, but used as such in the next step.

**3-Benzamido-2- $\gamma$ -benzyloxypropyl-4-carbomethoxyaminothiophene (Vb).**—A solution of 2 g. (0.00475 mole) of azide (IVb) in 30 ml. of absolute alcohol was refluxed on the steam-bath for seven hours. The brown solution was treated with Darco, filtered and the filtrate concentrated to one-half volume. Five volumes of water were added and the milky suspension stirred and cooled until crystals formed. Crystallization was allowed to proceed in the refrigerator overnight. The product when collected and dried weighed 1.87 g. (89% yield); m. p. 75–85°. Recrystallization from 66 $\frac{2}{3}$ % alcohol (by volume) gave 1.34 g. of white needles, m. p. 88–89°. Another crystallization raised the m. p. to 90–91°.

*Anal.* Calcd. for  $C_{24}H_{26}O_4N_2S$ : N, 6.39. Found: N, 6.41.

**2'-Keto-3,4-imidazolido-2- $\gamma$ -benzyloxypropylthiophene (VIb).**—The procedure was the same as that used for the preparation of the phenoxy compound (VIa). From 0.5 g. of the urethan (Vb) was obtained 0.231 g. (70.3% yield) of fine, colorless needles, m. p. 127–127.5°.

*Anal.* Calcd. for  $C_{15}H_{16}O_2N_2S$ : N, 9.71. Found: N, 9.66.

**2'-Keto-3,4-imidazolido-2- $\gamma$ -hydroxypropylthiophene (VIc).**—To a stirred solution of 1.32 g. (0.00458 mole) of the benzyl ether (VIb) in 100 ml. of liquid ammonia was added, in small pieces, 0.340 g. (0.0148 g. atom) of sodium. Immediately after the last piece of sodium had dissolved 0.790 g. (0.0148 mole) of ammonium chloride was added. Ammonia was allowed to evaporate at room temperature. The residue was extracted once with 25 ml. of dry ether to remove toluene which had been formed in the reaction. The residue was then placed in the thimble of a Soxhlet extractor and extracted with dry ether for seventy-two

hours. Evaporation of the ether left 0.775 g. (83.5% yield) of white material m. p. 131–133°. The compound crystallized from hot water in the form of needles, m. p. ca. 90°. This appeared to be a hydrated form since when dried in a pistol at 80° the needles disappeared and an amorphous product, m. p. 139–140°, was obtained.

*Anal.* Calcd. for  $C_{20}H_{10}O_2N_2S$ : C, 48.46; H, 5.08; N, 14.13; S, 16.17. Found: C, 48.56; H, 4.97; N, 13.93; S, 15.83.

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### Summary

2'-Keto-3,4-imidazolido-2- $\gamma$ -phenoxypropylthiophene (VIa) and 2'-keto-3,4-imidazolido-2- $\gamma$ -benzyloxypropylthiophene (VIb) have been synthesized from Ia and Ib, respectively, by means of the Curtius degradation.

2'-Keto-3,4-imidazolido-2- $\gamma$ -hydroxypropylthiophene (VIc) has been prepared from VIb by cleavage of the benzyl ether with sodium in liquid ammonia.

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[CONTRIBUTION FROM THE DIVISION OF PHYSIOLOGY, NATIONAL INSTITUTE OF HEALTH]

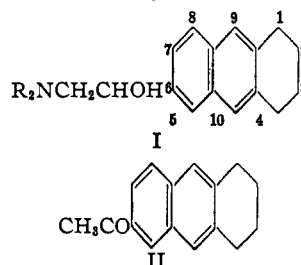
## Studies in the Anthracene Series. I. Methyl Ketones and Carbinolamines Derived from 1,2,3,4-Tetrahydroanthracene<sup>1</sup>

BY EDWARD A. GARLOCK, JR., AND ERICH MOSETTIG

In the course of an extended chemotherapeutic research program, the preparation of tetrahydroanthryl carbinolamines of formula I was warranted. The most convenient starting materials for these compounds are apparently the methyl ketones of which three aromatically substituted isomers are possible.

When, under mild conditions, 1,2,3,4-tetrahydroanthracene was allowed to react with acetyl chloride in the presence of aluminum chloride, a mixture of methyl ketones was obtained in a yield of about sixty to seventy per cent. One of the isomers could be separated readily by triturating the mixture with petroleum ether. It melts at 101–102°. By chromic acid oxidation it was converted to a quinone to which, by reasons of analogy,<sup>2</sup> the formula of an acetyltetrahydro-9,10-anthraquinone was assigned. On dehydrogenation with sulfur it yielded the known 2-acetylanthracene of m. p. 188–189.5°.<sup>3</sup> Moreover, it is oxidized with sodium hypochlorite to a tetrahydroanthracenecarboxylic acid whose ester is dehydrogenated to the corresponding 2-anthracene derivative. A migration of the acetyl or carbethoxyl group from position 1 to position 2 cannot be entirely excluded<sup>4</sup> but the moderate conditions of the dehydrogenation, together with the relatively high melting point of the tetrahydroacetyl compound support very strongly the assumption that no migration has taken place,

and that, therefore, the ketone of m. p. 101–102° is 6-acetyl-1,2,3,4-tetrahydroanthracene (II).



The oil remaining after separation of the crystalline ketone was purified repeatedly through the semicarbazone and picrate until a nearly colorless mobile oil of constant refractive index resulted. It gave on chromic acid oxidation a quinone to which, again by reasons of analogy,<sup>2</sup> the structure of an acetyltetrahydro-9,10-anthraquinone was assigned, and on dehydrogenation the known 1-acetylanthracene of m. p. 108°.<sup>4a,5</sup> In both operations the yields of pure end-product were rather low. Sodium hypochlorite oxidation of the carefully purified oily ketone, followed by esterification, gave an acid and its ester, respectively, which gave correct analytical results but had rather unsharp melting points in spite of repeated recrystallization. No explanation can be offered at present for this behavior. Moreover, the possibility that in the Friedel-Crafts reaction the hydrogenated ring was attacked cannot be overlooked entirely. Although other evidence indicates the probable structure of 5-acetyl-1,2,3,4-tetrahydroanthracene for the oily ketone, we suggest this as a tentative structure only. We expect to offer, within reasonable time, for this compound as well as for the solid ketone, an unambiguous structural proof. In the Friedel-Crafts reaction described above, nitrobenzene

(1) The work described in this paper was done in part under a contract, recommended by the Committee on Medical Research, between the Office of Scientific Research and Development and the National Institute of Health.

(2) 1,2,3,4-Tetrahydroanthracene is readily oxidized by chromic acid to 1,2,3,4-tetrahydro-9,10-anthracene quinone, ref. 6a. Meerwein and Migge, *Ber.*, **62**, 1046 (1929).

(3) (a) I. G. Farbenindustrie, A.-G., German Patents 492,247 and 493,688, *C. A.*, **24**, 2472, 2757 (1930); (b) Buu-Hoi and Cagniant, *Rec. trav. chim.*, **62**, 713 (1943).

(4) (a) Waldmann and Marmorstein, *Ber.*, **70**, 106 (1937); (b) I. G. Farbenindustrie, A.-G., German Patent 499,051; *C. A.*, **24**, 4055 (1930).

(5) King, *THIS JOURNAL*, **66**, 894 (1944). Reference 7.