

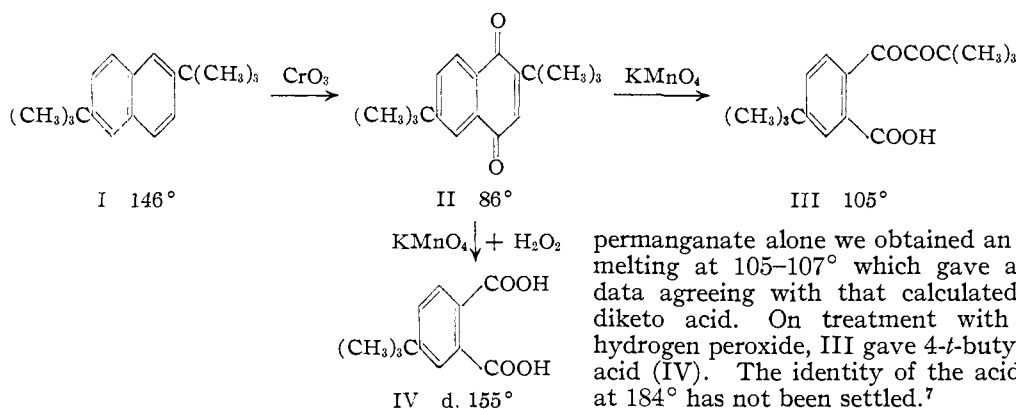
[CONTRIBUTION FROM THE SANDERS LABORATORY OF CHEMISTRY, VASSAR COLLEGE]

2,6-Di-*t*-butylnaphthalene¹BY H. MARJORIE CRAWFORD AND MARY CAROLYN GLESMANN²

RECEIVED SEPTEMBER 4, 1953

Of the two known di-*t*-butylnaphthalenes, the lower melting one has been shown to have the *t*-butyl groups in the 2,7-positions. Evidence is presented here to show that the higher melting hydrocarbon has the two *t*-butyl groups in the 2,6-positions.

Several earlier workers have shown that the reaction of *t*-butyl chloride with naphthalene in the presence of various condensing agents gives a mixture of 2-*t*-butylnaphthalene and two solid products melting at 146° and 80–82°. Price, *et al.*,³ showed that the lower melting material was a double compound made up of one molecule of the higher melting hydrocarbon (146°) and two molecules of another hydrocarbon melting at 103°. Fieser and Price⁴ described the oxidation of the 146° hydrocarbon I to the corresponding pale yellow quinone II.



Contractor, Peters and Rowe⁶ oxidized II (10 g.) with potassium permanganate followed by alkaline hydrogen peroxide and reported the formation of an acid (0.8 g.) melting at 184–185° which (solely on the basis of an analysis for carbon and hydrogen⁷) they suggested might be a di-*t*-butylphthalic acid. Since another possible oxidation product, a diketo acid, had almost the same per cent. composition as a di-*t*-butylphthalic acid it seemed advisable to try to prepare it and, by determining its neutral equivalent, decide whether it was a monobasic or a dibasic acid. When we oxidized II with potassium

permanganate alone we obtained an acid III, melting at 105–107° which gave analytical data agreeing with that calculated for the diketo acid. On treatment with alkaline hydrogen peroxide, III gave 4-*t*-butylphthalic acid (IV). The identity of the acid melting at 184° has not been settled.⁷

Work in our laboratory in 1948–49 showed that oxidation of the quinone II by potassium permanganate followed by hydrogen peroxide gave 4-*t*-butylphthalic acid (IV) which was sublimed to give the corresponding anhydride. This indicated that the two *t*-butyl groups in I were in different rings. Of the six possible structures for a di-*t*-butylnaphthalene with the substituents in different rings, the 1,5- and 1,8-arrangements could not yield 1,4-quinones. While 1,6- and 1,7-arrangements could give 1,4-quinones, oxidation of such quinones would yield 3-*t*-butylphthalic acid instead of 4-*t*-butylphthalic acid. This series of reactions thus left 2,6 or 2,7 for the positions of the two *t*-butyl groups in I.

In 1950 Nürsten and Peters⁵ showed that a compound known to be 2,7-di-*t*-butylnaphthalene is identical with the 103° hydrocarbon obtained from the double compound. This leaves the 2,6-arrangement for hydrocarbon I.

(1) Presented at the Fall Meeting of the American Chemical Society, Atlantic City, N. J., September, 1952.

(2) Taken in part from the thesis presented by Mary Carolyn Glesmann in partial fulfillment of the requirements for the degree of Master of Arts, June, 1949.

(3) C. C. Price, H. M. Shafer, M. F. Huber and C. Bernstein, *J. Org. Chem.*, **7**, 517 (1942).

(4) L. F. Fieser and C. C. Price, *THIS JOURNAL*, **58**, 1838 (1936).

(5) H. E. Nürsten and A. T. Peters, *J. Chem. Soc.*, 729 (1950).

Experimental

Preparation of 2,6-Di-*t*-butylnaphthalene (I).—The mixture of hydrocarbons was prepared by a modification of the procedure outlined by Gump.⁸ One mole (128 g.) of naphthalene was dissolved in two moles (185 g.) of *t*-butyl chloride with warming and mechanical stirring. As soon as the solid had dissolved the heating was discontinued and 1 g. of anhydrous aluminum chloride was added. When the vigorous reaction had subsided, another gram of aluminum chloride was added. The solution soon turned dark and, after the addition of 2–4 g. of aluminum chloride, solidified to a cream colored mass. After about 20 minutes the evolution of hydrogen chloride stopped and the solid was crystallized from methanol. The 146° hydrocarbon I separated first, an average yield being 74 g. Distillation of the methanol solution gave 45 g. of 2-*t*-butylnaphthalene (b.p. 280–290°) and 52 g. of the double compound (b.p. 320–340°, m.p. 80–82°). Recrystallization of this double compound from methanol gave more of the less soluble hydrocarbon I.

Preparation of 2,6-Di-*t*-butyl-1,4-naphthoquinone (II).—Half a mole (50 g.) of chromium trioxide dissolved in a mixture of 80 ml. of glacial acetic acid and 40 ml. of water was added slowly to a hot solution of 0.1 mole (24 g.) of I in 200 ml. of glacial acetic acid and the solution was refluxed for 15 minutes. The hot solution was poured onto ice and the filtered solid was crystallized from ethanol. Yields were 46–57% of pale yellow quinone, melting at 86–87°. Treatment of I with 30% hydrogen peroxide did not give the quinone.

(6) R. B. Contractor, A. T. Peters and F. M. Rowe, *ibid.*, 1993 (1949).

(7) Private communication from A. T. Peters.

(8) W. Gump, *THIS JOURNAL*, **53**, 380 (1931).

Preparation of 4-*t*-Butylphthalic Acid (IV).—A mixture of II (13.5 g.), potassium permanganate (27 g.) and water (500 ml.) was refluxed for three hours, cooled and filtered. The manganese dioxide was extracted with 75 ml. of 7% sodium hydroxide and this solution was combined with the original filtrate. After adding about 100 ml. of 3% hydrogen peroxide the mixture was allowed to stand overnight. The alkaline solution was extracted with ether and the ether layer discarded. Acidification of the aqueous layer, extraction with ether and evaporation of the ether gave 4.0 g. of the acid IV. Recrystallization from xylene removed the yellow contaminating material and IV separated in white, odorless crystals which melted with decomposition at 155–157°. Heating the oily residue with 5 ml. of aniline for about five minutes gave *N*-phenyl-4-*t*-butylphthalimide (5.6 g.) which was crystallized from ethanol. The total yield of acid from oxidation of the quinone was 76%, 36% as free acid and 40% as the imide.

Anal. Calcd. for $C_{12}H_{14}O_4$: neut. equiv., 111.1. Found: neut. equiv., 110.

When IV was heated it was converted into 4-*t*-butylphthalic anhydride which sublimed readily and melted at 77.5–78.5°. Both the acid and the anhydride gave positive fluorescein tests. Since the decomposition point of our acid was lower than the melting point reported by Bromby, Peters and Rowe⁹ and the melting point of our anhydride was higher, we repeated the preparation of the acid by the original method, the oxidation of 6-*t*-butyl-1,2,3,4-tetrahydronaphthalene. The resulting acid decomposed at 152°. Both samples of the acid, when heated with aniline, gave the same derivative, *N*-phenyl-4-*t*-butylphthalimide, melting points and mixed melting points 180–182°. Analysis for carbon and hydrogen agreed with the calculated values. Since our original preparation of *N*-phenyl-4-*t*-butylphthalimide in 1949, Lerner and Peters¹⁰ have prepared and described it.

Preparation of the Acid III.—A solution of 20 g. of potassium permanganate in 600 ml. of water was added with

(9) N. G. Bromby, A. T. Peters and F. M. Rowe, *J. Chem. Soc.*, 144 (1943).

(10) B. W. Lerner and A. T. Peters, *ibid.*, 680 (1952).

mechanical stirring to a boiling suspension of 10 g. of the quinone II in 300 ml. of water. The addition required six hours. After standing overnight the excess permanganate was destroyed by sodium bisulfite, the solution was made alkaline, filtered from manganese dioxide, and the acidified filtrate was extracted with ether. Removal of the ether left oily material which was crystallized from hexane containing a few drops of xylene. The white crystals melted at 105–107°; yield 30%.

Anal. Calcd. for $C_{17}H_{22}O_4$ (290): C, 70.3; H, 7.6. Found: C, 70.5; H, 7.8¹¹; neut. equiv., 304.

Two grams of the diketo acid III was treated with 10 ml. of 10% sodium hydroxide solution and 50 ml. of 3% hydrogen peroxide. The mixture became deep yellow in color and was allowed to stand overnight. By morning the color had disappeared and the acidified solution was extracted with ether. Evaporation of the ether left about 2.0 g. of oily acid which was converted to *N*-phenyl-4-*t*-butylphthalimide by heating with 2 ml. of aniline. The yield was 1.42 g., 72%.

Heating 0.6 g. of III with aniline gave no solid product.

Preparation of the Diacetate of 2-*t*-Butyl-1,4-naphthalenediol.¹²—This compound was prepared by the reductive acetylation of 2-*t*-butyl-1,4-naphthoquinone in 17% yield. The quinone was boiled for about ten minutes with excess zinc, sodium acetate and acetic anhydride. Pouring the clear solution into water precipitated a white solid which melted at 115–116° after crystallization from ethanol.

Anal. Calcd. for $C_{18}H_{20}O_4$: C, 72.0; H, 6.7. Found: C, 72.1; H, 6.7.

Hydrolysis of the diacetate and reduction of the quinone gave the hydroquinone which was not isolated as it is easily oxidized by the oxygen of the air.

(11) Analysis for carbon and hydrogen by Clark Microanalytical Laboratory, Urbana, Ill.

(12) From the thesis presented by Rose Marie Covey in partial fulfillment of the requirements for the degree of Master of Science, June, 1952.

POUGHKEEPSIE, NEW YORK

[CONTRIBUTION FROM THE STERLING-WINTHROP RESEARCH INSTITUTE]

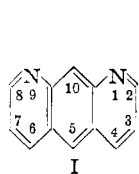
The Synthesis of Some 4,10-Disubstituted-1,7-phenanthroline Derivatives

BY ALEXANDER R. SURREY AND ROYAL A. CUTLER

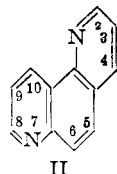
RECEIVED OCTOBER 22, 1953

The preparation of 4,10-dihydroxy-1,7-phenanthroline (VIII) from *m*-phenylenediamine by two methods is described. The hydroxy groups in VIII were replaced by chlorine to give either 4-chloro-10-hydroxy- or 4,10-dichloro-1,7-phenanthroline. The preparation of 4-, 10- and 4,10- basically substituted 1,7-phenanthroline derivatives is also reported.

In our search for new antimalarial agents, it seemed desirable to prepare some basically substituted pyridoquinoline compounds derived from *m*-phenylenediamine. The formation of two pyridine rings from appropriate derivatives of this diamine may proceed in two possible ways to give a benzodipyridine (I) or a 1,7-phenanthroline (II). In the present work, only derivatives of the angular structure II were obtained either by the Conrad-Limpach or Gould-Jacobs synthesis.



I



II

Condensation of *m*-phenylenediamine (III) (see Chart I) with two moles of ethyl oxalylacetate (IV)

gave 1,3-bis-(α,β -dicarbethoxyvinylamino)-benzene (V), which on cyclization in boiling Dowtherm led to the isolation of only a single diester in 40–50% yield. This product VI was hydrolyzed and the resulting dibasic acid VII was decarboxylated to give a dihydroxy compound VIII melting at 390°. Treatment of the latter with phosphorus oxychloride gave the corresponding dichloro derivative XIV from which the chlorines were removed by reductive dehalogenation to yield 1,7-phenanthroline, m.p. 76–77°. ¹

This would indicate that the structures assigned in the sequence III \rightarrow VIII are correct. That only the angular compound VI was obtained was not surprising since it is known that in the formation of cyclic compounds from phenylenediamine or quino-

(1) (a) Zd. H. Skraup and G. Vortmann, *Monatsh.*, **3**, 570 (1882), reported 1,7-phenanthroline as melting at 78–78.5°; (b) benzodipyridine has been found to melt much higher, 164.5–165° [P. Ruggli, P. Hindermann and H. Frey, *Helv. Chim. Acta*, **21**, 1066 (1938)].