[Contributions from the Chemical Laboratory of Harvard College.]

PHENYL HYDRAZONES OF α-ACETONAPHTHOL; ALKALI-INSOLUBLE NAPHTHOLS.

By Henry A. Torrey and C. M. Brewster.

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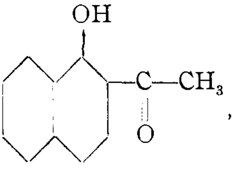
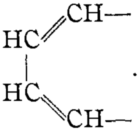
In an earlier communication by H. B. Kipper and one of us[1] it was shown that the phenyl hydrazones of certain oxyacetophenones were insoluble in aqueous alkalies. The alkali insolubility of these hydroxyl compounds was found to be due to the joint influence of the side chain, containing the phenylhydrazine residue $(CH_3.\underset{|}{C} = N.NHC_6H_5)$, *ortho* to the hydroxyl, and another group in the ring, as for instance the methoxy group. Thus while the phenyl hydrazones of resacetophenone, $\underset{(1)}{CH_3CO}C_6H_3\underset{(2)}{OH}.\underset{(4)}{OH}$, and of *o*-hydroxy-acetophenone are readily soluble in aqueous alkalies, the phenylhydrazone of paeonol, $\underset{(1)}{CH_3CO}C_6H_3\underset{(2)}{OH}\text{-}\underset{(4)}{OCH_3}$, is insoluble. The present paper containing observations on α-acetonaphthol,  , establishes the alkali insolubility of its phenyl hydrazones, which is due in this case to the joint influence of the $CH_3\underset{|}{C} = N.NHC_6H_5$ group in the ortho position to the hydroxyl *and* of the hydrocarbon residue,  . These hydrazones furnish excellent examples of this alkali insolubility, as they are very stable and may be boiled with strong aqueous alkalies without change; the deep red *m*-nitrophenylhydrazone of α-acetonaphthol, for instance, imparts practically no color to the alkali under this treatment. The presence of a bromine atom in the naphthalene ring or in the phenyl group has no influence on the solubility.

Experimental Part.

α-Acetonaphthol was prepared according to Friedländer's method[2] by heating α-naphthol with a mixture of 1½ parts of zinc chloride and 1½ parts glacial acetic acid for 15–20 minutes at 145–150°. The product was poured into water acidified with hydrochloric acid, washed with very dilute hydrochloric acid, and purified by repeated crystallization from 80 per cent. acetic acid until the purple by-product was removed, and by final crystallization from hot alcohol, m. p. 102°. When crystallized from alcohol, α-acetonaphthol consists of pale green needle-shaped crystals. It is

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[1] This Journal, 30, 836 (1908).

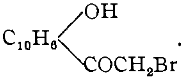
[2] *Ber.*, **28**, 1946.

readily soluble in ether, benzene and ligroïn, but more difficultly soluble in alcohol and acetic acid. On heating α-acetonaphthol with a sodium hydroxide solution and adding a little alcohol, the sodium salt is formed, which is difficultly soluble in water, but more easily in alcohol.

Mono-brom-α-acetonaphthol, $C_{10}H_5OH.Br.COCH_3$, was prepared by dissolving acetonaphthol in warm alcohol and pouring it into a warm alcoholic solution of somewhat more than one molecule of bromine. The mixture was stirred rapidly, and kept warm for ten minutes. The bromacetonaphthol crystallizes out almost immediately. It was purified by numerous crystallizations from glacial acetic acid and from alcohol and was obtained in the form of yellow-green crystals of constant melting point, 126–7°. It is soluble in ether, benzene, ligroïn, carbon tetrachloride, chloroform, carbon disulphide and aniline.

Calculated for $C_{12}H_9OBr$: Br, 30.18
Found: Br, 30.25, 30.35

G. Ullmann[1] describes a mono-bromo derivative of α-acetonaphthol melting at 124.5°, obtained by bromination in carbon tetrachloride in which he believes the bromine to have replaced a hydrogen of the methyl group,

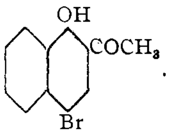


$C_{10}H_6\begin{cases} OH \\ COCH_2Br \end{cases}$.

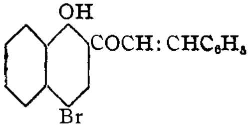
Ullmann's description of the preparation of this body does not make it quite clear whether the bromination was carried out on the acetonaphthol itself or on its acetyl derivative. We judge, however, that he used the latter body, as in another place in his article he says that it is impossible to introduce a bromination into the side chain in the non-acetylated body. That Ullmann succeeded in obtaining bromine derivatives in which a halogen has replaced a hydrogen of the methyl group is shown by his formation of naphtho-keto-cumaran from such a substitution product by the action of alkalies. We have carried out the bromination of the free α-acetonaphthol in carbon tetrachloride and obtained the same mono-bromo derivative as was formed when the reaction took place in alcoholic solution.

That in the bromacetonaphthol described by us the bromine has replaced a hydrogen in one of the rings and not in the side chain is shown by the fact that it is not decomposed by warming with a sodium hydroxide solution for two hours. On cooling, yellow plates of the sodium salt of bromacetonaphthol separated and from the filtrate on acidification unchanged bromacetonaphthol was obtained, melting at 125–8°.

Since in the nitration of acetonaphthol the nitro group enters the para position,[2] it is highly probable that the bromacetonaphthol is also a para derivative as represented in the following formula:



Further evidence that the bromine atom is not in the side chain is furnished by the formation of a benzylidine derivative containing bromine, by the action of benzaldehyde and sodium hydroxide on acetonaphthol, which may be represented thus:



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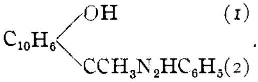
[1] *Ber.*, 30, 1468.

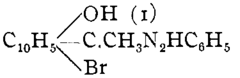
[2] *Ibid.*, 28, 1948.

Condensation of Bromacetonaphthol and Benzaldehyde. Benzylidine bromacetonaphthol, $C_{10}H_5OHBrCOCH:CHC_6H_5$.—The two substances dissolved in alcohol were mixed with some 10 per cent. sodium hydroxide and heated for some time. Small pieces of solid sodium hydroxide were added from time to time, until the solution began to grow dark. On acidifying the cold solution, a red precipitate separated out. This was purified by crystallization from glacial acetic acid and gave an orange colored crystalline product, with a melting point of 176–177°, soluble in carbon tetrachloride, benzene, aniline, acetone, carbon disulphide, and hot ligroïn; difficultly soluble in alcohol, ether, and glacial acetic acid.

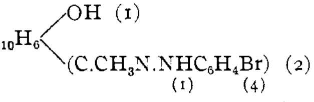
Calculated for $C_{19}H_{13}O_2Br$:	Bromine = 22.66
Found:	Bromine = 23.00, 22.60

Acetonaphthol phenylhydrazone,  $C_{10}H_6\left\langle\begin{matrix}OH\quad(1)\\ CCH_3N_2HC_6H_5(2)\end{matrix}\right.$.—This hydrazone was formed by heating for two hours an alcoholic solution of acetonaphthol with a little more than one molecule of phenylhydrazine in the presence of a small amount of acetic acid. When the solution was slightly diluted with water, crystals slowly separated which were purified by repeated crystallization from dilute alcohol. The pure substance consists of white needle-like crystals, melting at 136–7°, which tend to turn brown on standing. It is soluble in glacial acetic acid, alcohol, ether, carbon tetrachloride, chloroform, carbon disulphide, hot ligroïn, and hot aniline, but insoluble in aqueous sodium hydroxide.

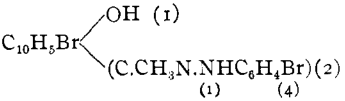
Calculated for $C_{18}H_{16}N_2O$:	N, 10.14.
Found:	N, 10.18, 10.07.

Bromacetonaphthol phenylhydrazone,  $C_{10}H_5\left\langle\begin{matrix}OH\ (1)\\ C.CH_3N_2HC_6H_5\ (2)\\ Br\end{matrix}\right.$.—This body was prepared by heating an alcoholic solution of one molecule of bromacetonaphthol with one molecule of phenylhydrazine in presence of acetic acid, as in the preparation of the phenylhydrazone of acetonaphthol. It crystallized from alcohol in pale yellow needles, decomposing at 159°. It is soluble in alcohol, carbon tetrachloride, carbon disulphide, benzene, chloroform, ether, and ligroïn. Its insolubility in aqueous sodium hydroxide was shown by allowing it to stand three days with the alkali without its being dissolved. It is very noticeably affected by light, changing in a short time in direct sunlight from a light yellow color to rather deep brown.

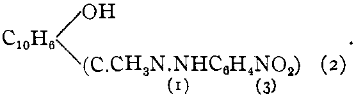
Calculated for $C_{18}H_{15}N_2OBr$:	Br, 22.53;	N, 7.88.
Found:	Br, 22.73, 23.23;	N, 7.84.

Acetonaphthol p-bromophenylhydrazone,  $C_{10}H_6\left\langle\begin{matrix}OH\ (1)\\ (C.CH_3N.\underset{(1)}{N}HC_6H_4\underset{(4)}{Br})\ (2)\end{matrix}\right.$.—An alcoholic solution of acetonaphthol was boiled with an excess of *p*-bromophenylhydrazine for one hour in the presence of acetic acid. On cooling, silvery-white plates of the condensation product separated from solution, which were purified by recrystallization from glacial acetic acid. The compound melts at 185–6°, and is soluble in alcohol, benzene, carbon tetrachloride, ether, chloroform, aniline, and acetone; difficultly soluble in acetic acid and ligroïn and entirely insoluble in concentrated aqueous sodium hydroxide, even after continued boiling. It may be crystallized from hot glacial acetic acid or from acetone and alcohol.

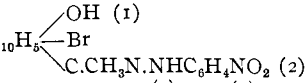
Calculated for $C_{18}H_{15}ON_2Br$, Br 22.53; found, Br 23.16.

Bromacetonaphthol p-bromophenylhydrazone,  $C_{10}H_5Br\begin{cases}OH\ (1)\\ (C.CH_3N.NHC_6H_4Br)(2)\\ \qquad\ \ (1)\qquad\ \ (4)\end{cases}$ —The same method was used as for the preceding compound, using bromacetonaphthol instead of acetonaphthol. On cooling the reaction mixture, an oily mass separated out from the clear solution, which, however, becomes solid on standing. Almost colorless crystals were obtained by crystallizing from acetic acid, which melted with decomposition at 160°. This hydrazone is soluble in alcohol, carbon tetrachloride, chloroform, benzene, ether, aniline and acetone, and more difficultly soluble in ligroïn and acetic acid. It is insoluble in a boiling concentrated sodium hydroxide solution.

Calculated for $C_{18}H_{14}ON_2Br_2$, Br 36.86; found, Br 36.93.

Acetonaphthol m-nitrophenylhydrazone,  $C_{10}H_6\begin{cases}OH\\ (C.CH_3N.NHC_6H_4NO_2)\ (2)\\ \qquad\ (1)\qquad\ \ (3)\end{cases}$.—When the alcoholic solution of acetonaphthol is boiled for one hour with *m*-nitrophenylhydrazine in the presence of acetic acid a deep red solution results, and on addition of water a red precipitate falls. When purified by repeated crystallization from glacial acetic acid, the compound is obtained in the form of deep red compact needles which melt with decomposition at 232–3°. It is soluble in alcohol, benzene, chloroform, acetone, and aniline, somewhat less soluble in acetic acid, ether and carbon disulphide and insoluble in carbon tetrachloride and ligroïn. It is insoluble in aqueous alkalies. Even after boiling with a sodium hydroxide solution only the slightest tinge of color was communicated to the liquid.

Calculated for $C_{18}H_{15}N_3O_3$, N 13.08; found, 12.94.

Bromacetonaphthol m-nitrophenylhydrazone,  $C_{10}H_5\begin{cases}OH\ (1)\\ Br\\ C.CH_3N.NHC_6H_4NO_2\ (2)\\ \qquad\ (1)\qquad\ \ (3)\end{cases}$ —When bromacetonaphthol dissolved in hot glacial acetic acid is boiled with *m*-nitrophenylhydrazine for one hour, an orange-red precipitate is formed, which on purification by crystallization from hot acetone and alcohol gives deep orange crystals which melt with decomposition at 201–4°. It is readily soluble in hot acetone and aniline, difficultly soluble in benzene and hot glacial acetic acid, and insoluble in alcohol, ether, and ligroïn. It is not changed by heating with an aqueous sodium hydroxide solution, but like alkali-insoluble phenols in general, it is dissolved by *alcoholic* sodium hydroxide. The presence of the bromine atom in the naphthalene ring seems to lighten the color of these nitrophenylhydrazones considerably, as this bromacetonaphthol nitrophenylhydrazone is orange, while the corresponding derivative of acetonaphthol itself is deep red.

Calculated for $C_{18}H_{14}BrO_3N_3$, Br 20.00; found, 19.64.

We are continuing this work on alkali-insoluble naphthols and similar compounds.

CAMBRIDGE, MASS.