peared to be no reason to expect it to be unstable to potassium cyanide. This was verified by heating thiophene with potassium cyanide in aqueous alcohol. The thiophene was recovered unchanged.

The acyloin condensation of 2-thiophenealdehyde to thenoin was effected by boiling the aldehyde with a solution of potassium cyanide in aqueous alcohol and neutralizing the reaction mixture. Thenoin was oxidized to thenil by the action of copper sulfate in dilute pyridine solution and thenil was converted to thenilic acid by the action of alcoholic potassium hydroxide.

Experimental

2-Thiophenealdehyde.—This aldehyde was prepared from 2-chloromethylthiophene by the method of Dunn, Waugh and Dittmer.[3] The 2-chloromethylthiophene was prepared by the chloromethylation of thiophene by the method of Blicke and Burckhalter.[4] In this preparation it was found that concentrated hydrochloric acid at a temperature of 20–25° could be used, instead of gaseous hydrogen chloride at 0–5°, without lowering the yield.

2,2′-Thenoin.—A solution of 3 g. of potassium cyanide in 20 cc. of water was added to a solution of 25 g. of thiophenealdehyde in 40 cc. of alcohol. The mixture darkened immediately. It was boiled for a half hour, allowed to cool, and acidified with 5 cc. of concentrated hydrochloric acid. The dark green solution turned light yellow in color and on standing deposited brown crystals. These were filtered off and recrystallized from alcohol using decolorizing charcoal. Eight grams, a yield of 32%, of white crystals, m. p. 107–108°, was obtained.

Anal. Calcd. for $C_{10}H_{9}O_{2}S_{2}$: S, 28.54. Found: S, 28.43.

Thenoin rapidly reduces Fehling solution and Tollens reagent. Like benzoin, an alcohol solution is colored deep green upon adding a drop of dilute alkali and the color disappears temporarily upon shaking. The oxime, prepared by the action of hydroxylamine in pyridine, is a white crystalline solid, m. p. 142–143°.

Anal. Calcd. for $C_{10}H_{9}O_{2}S_{2}N$: S, 26.78. Found: S, 26.86.

2,2′-Thenil.—Thenil was obtained by the oxidation of thenoin by the method used by Hartman and Dickey[5] for the preparation of furil from furoin. Fifteen grams of copper sulfate was dissolved in a mixture of 21 g. of pyridine and 10 g. of water on a steam-bath. Six grams of thenoin was added and the mixture heated on a steam-bath, with stirring, for two hours. The mixture was poured into water and the thenil precipitated as a black solid. It was filtered, washed free of copper salts, and was recrystallized from methyl alcohol using charcoal. Two grams of yellow needles, a 33% yield, melting at 83–84° was obtained.

Anal. Calcd. for $C_{10}H_{6}O_{2}S_{2}$: S, 28.83. Found: S, 28.73.

2,2′-Thenilic Acid.—Three grams of thenil was added to a solution of 3 g. of potassium hydroxide in 50 cc. of 50% alcohol. The mixture was allowed to stand overnight at room temperature and was then poured into 100 cc. of water. The solution was carefully neutralized with hydrochloric acid and a tarry precipitate settled out and was filtered off. The filtrate was extracted with ether, the ether extract was evaporated to a small volume, and then shaken with 100 cc. of water. One and one half grams, a yield of 45%, of grayish white crystals separated out and were dried in a desiccator. The thenilic acid darkened rapidly on standing and decomposed, without melting, at about 80°.

Anal. Calcd. for $C_{10}H_{8}O_{3}S_{2}$: S, 26.7; neut. equiv., 240. Found: S, 26.8; neut. equiv., 241.

An attempt to prepare thenilic acid from thenoin by the method of Ballard and Dehn[6] for the preparation of benzilic acid from benzoin, gave only 2,2′-dithienyl ketone, m. p. 88°.

---

[3] Dunn, Waugh and Dittmer, This Journal, **68**, 2118 (1946).

[4] Blicke and Burckhalter, *ibid.*, **64**, 477 (1942).

[5] Hartman and Dickey, *ibid.* **55**, 1228 (1933).

[6] Ballard and Dehn, "Organic Syntheses," Collective Vol. I. 2nd ed., John Wiley and Sons, Inc., New York, N. Y., 1941, p. 89.

MORLEY CHEMICAL LABORATORY
WESTERN RESERVE UNIVERSITY
CLEVELAND 6, OHIO

RECEIVED JULY 2, 1948

The Identity of "x-Benzylphenanthrene"

BY WILLIAM A. BONNER AND ANNE MOSHER

In 1881 Goldschmiedt[1] prepared a hydrocarbon, $C_{21}H_{16}$, m. p. 155–156°, by heating a mixture of phenanthrene, benzyl chloride and zinc dust. He offered no proof of structure for this product, and referred to it merely as benzylphenanthrene. In Beilstein's "Handbuch" it is listed as "x-benzylphenanthrene," and heretofore no one has attempted to locate the position of the benzyl group in Goldschmiedt's product. In connection with another problem we became interested in the structure of this substance.

In 1934 Bachmann[2] gave an unequivocal synthesis of 9-benzylphenanthrene, m. p. 153–154°, by the action of benzyl chloride on 9-phenanthrylmagnesium bromide. A substance believed to be 9-benzylphenanthrene, m. p. 91–92°, had been previously prepared by Willgerodt and Albert[3] by reduction of the supposed 9-benzoylphenanthrene resulting from the Friedel–Crafts acylation of phenanthrene with benzoyl chloride. In an extensive synthetic study Bachmann later showed[4] that the structures of Willgerodt's products were in error, but the possible identity of authentic 9-benzylphenanthrene with Goldschmiedt's "x-benzylphenanthrene" was apparently not considered.

We have repeated the reactions of Goldschmiedt and Bachmann with essentially their results. The products from these two reactions had identical melting point and showed no mixed melting point depression. Their identity was further established by measurement of their absorption spectra which, as seen in Fig. 1, proved remarkably similar.

Experimental

9-Benzylphenanthrene.—This was prepared in 52% crude yield by refluxing benzyl chloride with a benzene and ether solution of 9-phenanthrylmagnesium bromide after the method of Bachmann.[2] After extensive recrystallization from benzene the pure product was obtained, m. p. 155–156°.

"x-Benzylphenanthrene."—In the preparation of this product the essential reaction conditions of Goldschmiedt[1] were employed, but the method of isolating the product was varied slightly. Phenanthrene (32 g., 0.179 mole, m. p. 99–100.5°), benzyl chloride (44 g., 0.346 mole) and zinc dust (10 g., 0.153 mole) were mixed and heated on the steam-bath for one and one-half hours. The

---

[1] Goldschmiedt, *Monatsh.*, **2**, 444 (1881).

[2] Bachmann, This Journal, **56**, 1363 (1934).

[3] Willgerodt and Albert, *J. prakt. Chem.*, [2] **84**, 383 (1911).

[4] Bachmann, This Journal, **57**, 555 (1935).

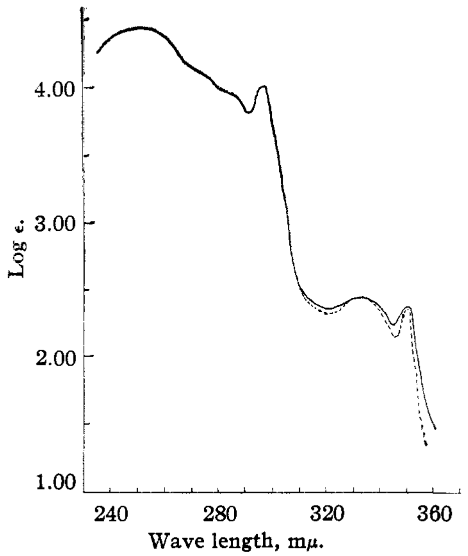


Fig. 1.—Absorption spectra of benzylphenanthrenes: —, 9-benzylphenanthrene, -----------, x-benzylphenanthrene.

bluish, fluorescent oil obtained was dissolved in benzene and the solution filtered from the inorganic residue. The benzene was distilled, and on standing one day the residue deposited yellow crystals. These were collected, treated with hot alcohol, and the insoluble portion recrystallized from benzene to give, on processing the mother liquors and alcohol extract for further material, a total of 0.36 g. of impure "x-benzylphenanthrene." The original residue from the benzene solution was distilled at 3.5 mm. in a distilling flask equipped with a short, wide side-arm. The first fraction (1.6 g., b. p. 130–160°, bath temp. 200–214°) crystallized in the side-arm and was melted into the receiver. The second fraction (29.6 g., b. p. 160–305°, bath temp. 214–335°) distilled as a yellow oil which slowly solidified in the receiver. A large amount of material (18.6 g.) had not distilled when the bath reached 335°. The first fraction, on several recrystallizations from ethanol, proved to be impure phenanthrene. The second fraction was found sparingly soluble in alcohol, but could be dissolved in 40 ml. of benzene. On chilling 5.9 g. of yellow crystals deposited, m. p. 124.5–140.5°. Recrystallization from benzene resulted in 1.0 g. of lighter material, m. p. 147–151°. After several additional recrystallizations from benzene pure "x-benzylphenanthrene" was obtained, m. p. 155–156°. These showed no m. p. depression (155–156°) when mixed with the 9-benzylphenanthrene prepared above.

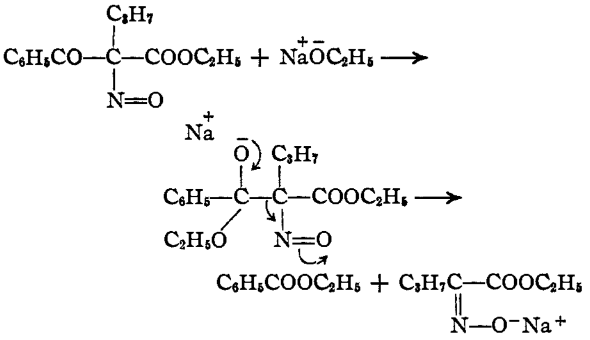
Absorption Spectra.—The spectra of the two compounds prepared above were measured in 95% ethanol at a concentration of 10^{-4} molar with a Model DU Beckman Quartz Spectrophotometer using the ultraviolet photo cell and the hydrogen lamp light source. Readings were taken at intervals of 5 mμ except in regions of maximum curvature where readings were taken at intervals of 1 or 2.5 mμ.

STANFORD UNIVERSITY
STANFORD, CALIF. RECEIVED AUGUST 11, 1948

Cleavage of Nitrosated β-Keto Esters to Form α-Oximino Esters

BY CHARLES R. HAUSER AND GEORGE A. REYNOLDS

Suitable methods for the synthesis of α-oximino acid esters, which may be reduced to α-amino acid esters include the nitrosation of alkylated malonic esters and alkylated acetoacetic esters followed by cleavage with sodium ethoxide.[1,2] The mechanism for the cleavage of the nitrosated malonic esters was discussed recently.[1] The mechanism for the cleavage of nitrosated β-keto esters is here considered. For the present purpose ethyl α-benzoylvalerate[3] was employed. This alkylated benzoylacetic ester, on treatment with ethyl nitrite and sodium ethoxide, produced ethyl benzoate (70%) in addition to the oximino ester, ethyl α-oximinovalerate (75%), which was subsequently reduced to the α-amino ester, ethyl α-aminovalerate. The mechanism for the cleavage of the nitroso derivative, which is presumably formed as an intermediate, may be represented as



$$C_6H_5CO{-}\overset{\displaystyle C_3H_7}{\underset{\displaystyle N{=}O}{C}}{-}COOC_2H_5 + \overset{+}{Na}\overset{-}{O}C_2H_5 \longrightarrow$$

$$\overset{+}{Na}\quad C_6H_5{-}\overset{\displaystyle \overset{-}{O}}{\underset{\displaystyle C_2H_5O}{C}}{-}\overset{\displaystyle C_3H_7}{\underset{\displaystyle N{=}O}{C}}{-}COOC_2H_5 \longrightarrow$$

$$C_6H_5COOC_2H_5 + C_3H_7\underset{\displaystyle N{-}O^-Na^+}{\overset{\Vert}{C}}{-}COOC_2H_5$$

Procedure.—In a flat bottle equipped with a mercury-sealed stirrer, ice-water cooled condenser (drying tube) and dropping funnel was placed 23.4 g. (0.1 mole) of ethyl benzoylvalerate. After cooling to 0°, 12 g. (0.13 mole) of ethyl nitrite was added to the stirred solution. The mixture was cooled to −10° in an ice–salt-bath and 0.1 mole of sodium ethoxide (prepared from 2.3 g. of sodium and 45 ml. of absolute ethanol) was added slowly with stirring. The flask was stoppered and placed in the freezing unit of a refrigerator for twelve hours. The mixture was poured into an evaporating dish and kept in a vacuum desiccator over concentrated sulfuric acid until the alcohol had evaporated. To the residue was added an equal volume of ice-water and the resulting mixture was extracted with ether. From the ether solution, after drying and removing the solvent, there was obtained 10.2 g. (70%) of ethyl benzoate which was identified by its boiling point and by hydrolysis to benzoic acid. The cooled aqueous solution was acidified to a *p*H of 5 with ice-cold concentrated hydrochloric acid and extracted three times with ether. Solid potassium carbonate was added to the aqueous solution which was extracted with ether at a *p*H of 7 and again at a *p*H of 9. The combined ether extracts were dried over Drierite and the solvent distilled yielding 12 g. (75%) of ethyl α-oximinovalerate as a white solid, m. p. 47–48°. The product boiled at 123–124° at 5 mm.[4]

The oximino ester (5 g., 0.03 mole) in 50 ml. of commercial absolute ethanol was hydrogenated at 85° over Raney nickel (1 g.) at 900 pounds pressure. After filtering off the Raney nickel and distilling the alcohol, the residue was fractionated yielding 3 g. (69%) of ethyl α-aminovalerate boiling at 74–75° at 8 mm.

DEPARTMENT OF CHEMISTRY
DUKE UNIVERSITY RECEIVED AUGUST 9, 1948
DURHAM, NORTH CAROLINA

---

[1] See Shivers and Hauser, THIS JOURNAL, **69**, 1264 (1947).

[2] See Barry and Hartung, *J. Org. Chem.*, **12**, 460 (1947).

[3] This β-keto ester (b. p. 143° at 2 mm.) was prepared in 74% yield by the alkylation of ethyl benzoylacetate with *n*-propyl iodide; see Calman, *J. Chem. Soc.*, **49**, 160 (1886).

[4] Schmidt and Dieterle, *Ann.*, **377**, 48 (1910).