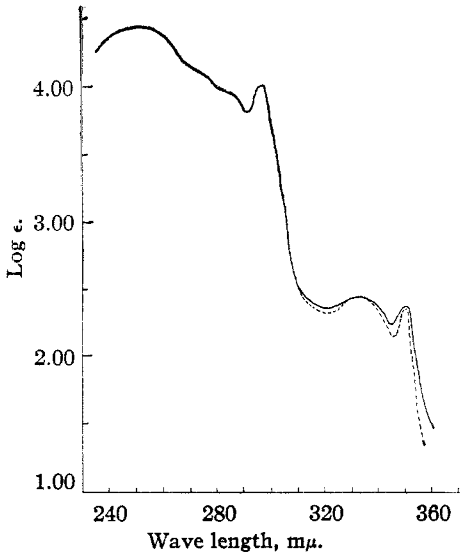

Fig. 1.—Absorption spectra of benzylphenanthrenes: —, 9-benzylphenanthrene, -----------, x-benzylphenanthrene.

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.

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

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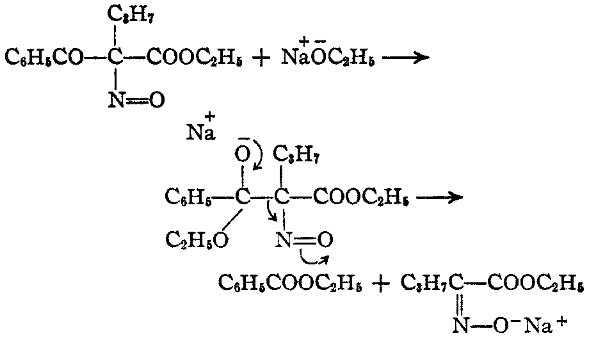
Suitable methods for the synthesis of α-oximino acid esters, which may be reduced to α-amino acid esters include the nitrosation of alkylated malonic esters and alkylated acetoacetic esters followed by cleavage with sodium ethoxide.[1,2] The mechanism for the cleavage of the nitrosated malonic esters 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



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.

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[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).