2-(1-Benzyloximino-2-phenylethyl)-4-benzaloxazolone. In a 100-ml. flask was placed a mixture of 1.0 g. (0.0095 mole) benzaldehyde, 3.45 g. (0.0107 mole) of powdered α-benzyloximino-β-phenylpropionylglycine, 0.8 g. of freshly fused and powdered sodium acetate, and 2.5 ml. acetic anhydride. The contents were heated as described above and the product isolated in a similar manner. The crude product weighed 3.0 g., m.p. 154–156° (uncorr.); recrystallized from ligroin, m.p. 155–156° (uncorr.).

Anal. Calcd. for $C_{25}H_{20}N_2O_3$: N, 7.07. Found: N, 8.02, and 8.00.

N-(α-Benzyloximino-β-phenylpropionyl)-α-aminocinnamoylglycine. A hundredth mole glycine (0.75 g.) was dissolved in 10 ml. normal NaOH solution and added to a suspension of 0.01 mole (3.96 g.) of 2-(1-benzyloximino-2-phenylethyl)-4-benzaloxazolone in 30 ml. acetone, and the mixture shaken continuously for about 30 min., at which time the azlactone was completely dissolved. The mixture was allowed to stand overnight, filtered, and then acidified with hydrochloric acid, and the solvent allowed to evaporate at room temperature. A white solid, with some oil which solidified on scratching, remained; recrystallized from dilute alcohol, white crystals were formed, 3.5 g., m.p. 144°.

Anal. Calcd. for $C_{27}H_{27}N_3O_5$: N, 8.91. Found: N, 8.95, 8.97.

N-(α-Methyloximino-β-phenylpropionyl)-α-aminocinnamoylglycine. This compound was prepared in a manner similar to the benzyloximino analog in yield of 75%; recrystallized from dilute acetone, it melted 156–157°.

Anal. Calcd. for $C_{21}H_{21}N_3O_5$: N, 10.73. Found: N, 10.14, 10.30.

DL-*Phenylalanylphenylalanylglycine.* To a solution of 97 ml. water and 3 ml. concentrated ammonia was added 2.64 g. (0.006 mole) of *N*-(α-methyloximino-β-phenylpropionyl)-α-aminocinnamoylglycine and catalyst prepared from 2 g. charcoal and 200 mg. $PdCl_2$. Hydrogenation was carried out in a Parr apparatus at about 4 atm. hydrogen pressure. The first H_2 was taken up in about 50 min., the second H_2 in about 3 hr., and the remainder in 20 hr. The catalyst was removed by filtration and the filtrate concentrated on a hot water bath at reduced pressure; the residue was taken up in a small amount of hot water and filtered to remove insoluble material. The colored solid obtained from the aqueous solution was crystallized from 50% alcohol and, after drying *in vacuo* at 100° over P_2O_5 for 8 hr. weighed 1.22 g., 66% of theory, discolored at 195° and melted with decomposition at 203–213°.

Anal. Calcd. for $C_{20}H_{23}N_3O_4$: C, 65.02; H, 6.25; N, 11.37. Found[7]: C, 64.95; H, 6.32; N, 11.22.

Benzoyl derivative, recrystallized from dilute alcohol, m.p. 222–223°.

Anal. Calcd. for $C_{27}H_{27}N_3O_5$: N, 8.87. Found: N, 8.62, 8.58.

The hydrogenation of *N*-(α-benzyloximino-β-phenylpropionyl)-α-aminocinnamoylglycine under similar condition gave 62% yield of the tripeptide, which, in physical properties and *N*-benzoyl derivative, was identical with DL-phenylalanylphenylalanylglycine.

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(7) Analyses by Micro-Tech Laboratories, Skokie, Ill.

A New Method for Synthesis of Higher α,ω-Diarylated Fatty Acids

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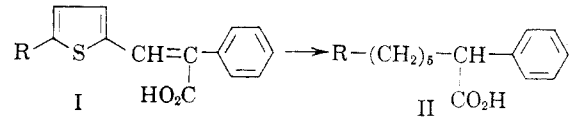
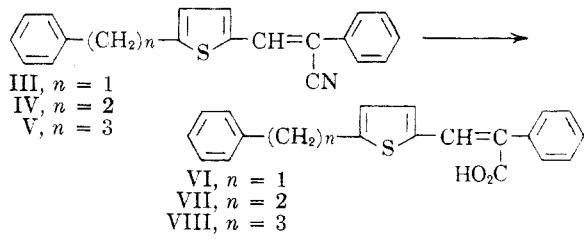
During the past five years, numerous reports have appeared concerning the synthesis of aliphatic,[1] alicyclic,[2] and aromatic[3] carboxylic acids by hydrogenolysis of suitably substituted thiophenes with Raney nickel-aluminum alloy in alkaline medium. Buu-Hoï and Sy[4] recently reported a method for the preparation of α-alkylated phenylacetic acids (II) by hydrogenolyses of that type, involving α-phenyl-β-(2-thienyl)acrylic acids of general formula I; in these reactions, the saturation

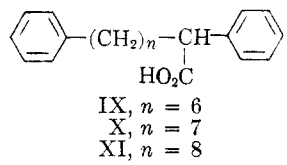


of the double bond occurred simultaneously with the reductive opening of the thiophene ring. The present work records an extension of this reaction to the preparation of higher fatty acids containing two phenyl radicals in the α and ω positions, and which were hitherto unknown.

The alkali-catalyzed condensation of 5-benzyl-2-thenaldehyde[5] with benzyl cyanide readily gave α-phenyl-β-(5-benzyl-2-thienyl)acrylonitrile (III),



which was hydrolyzed to the corresponding acid (VI), and hydrogenolysis of this latter afforded α,ω-diphenylcaprylic acid (IX). α-Phenyl-β-(5-β-phenylethyl-2-thienyl)acrylonitrile (IV), prepared from 5-β-phenylethyl-2-thenaldehyde,[6] was



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successfully converted to α,ω-diphenylpelargonic acid (X) in the same way, *via* the acrylic acid VII. Similarly, α,ω-diphenylcapric acid (XI) was prepared from α-phenyl-β-(5-γ-phenylpropyl-2-thienyl)acrylonitrile (V), the latter compound being synthesized from 5-γ-phenylpropyl-2-thenaldehyde.

In view of the ready availability of the thiophene aldehydes as intermediates, and despite the low over-all yields, the present method seems to offer a more convenient route to α,ω-diarylated higher fatty acids than the routine malonic syntheses.

EXPERIMENTAL

Preparation of intermediates. 2-Benzyl- and 2-β-phenylethylthiophene were prepared by applying the Huang-Minlon modification[7] of the Kishner-Wolff reaction to 2-benzoyl- and 2-phenacetylthiophene. 2-β-Phenylpropionylthiophene, prepared by a stannic chloride-catalyzed Friedel-Crafts reaction of β-phenylpropionyl chloride with thiophene,[8] was similarly reduced to 2-γ-phenylpropylthiophene,[9] a pale yellow oil, b.p. 288–289°, n_D^{19} 1.5798; the yield of the reduction was 60%.

Formylation of these arylalkylthiophenes was effected by means of dimethylformamide and phosphorus oxychloride; *5-γ-phenylpropyl-2-thenaldehyde* thus prepared was a pale yellow oil, b.p. 222–225°/19 mm. (69% yield).

Anal. Calcd. for $C_{14}H_{14}OS$: C, 73.0; H, 6.1. Found: C, 72.8; H, 6.2.

α-Phenyl-β-(5-benzyl-2-thienyl)acrylic acid (VI). The hydrolysis of the corresponding nitrile[9] was effected either by prolonged heating (72 hr.) with a solution of sodium hydroxide in propanol or butanol, or, more rapidly and with similar yields, by the sulfuric acid method. Acid VI crystallized from ethanol in shiny, colorless leaflets, m.p. 139°; yield: 55-65%.

Anal. Calcd. for $C_{20}H_{16}O_2S$: C, 75.0; H, 5.0. Found: C, 74.9; H, 5.0.

α,ω-Diphenylcaprylic acid (IX). To a solution of the foregoing acid (4 g.) in a 10% aqueous solution of sodium hydroxide heated on a water bath, a large excess of Raney alloy of nickel and aluminum (20 g.) was added in small portions with stirring, and heating was continued for a further thirty minutes. After cooling, the precipitate of nickel was filtered off and washed several times with hot water; the filtrate was acidified with hydrochloric acid, the reduction product taken up in benzene, the benzene solution washed with water then dried over sodium sulfate, and the solvent removed. The residue was recrystallized several times from petroleum ether, giving colorless prisms, m.p. 65°; yield: 74%.

Anal. Calcd. for $C_{20}H_{24}O_2$: C, 81.1; H, 8.1. Found: C, 81.0; H, 8.0.

α-Phenyl-β-(5-β-phenylethyl-2-thienyl)acrylonitrile (IV). An equimolar mixture of 5-β-phenylethyl-2-thenaldehyde and benzyl cyanide in ethanol was shaken for a few minutes with a few drops of 20% aqueous sodium hydroxide; the oily precipitate which formed on dilution with water, solidified on standing in the refrigerator. Recrystallization from ethanol afforded an 87% yield of shiny, yellowish prisms, m.p. 111°.

Anal. Calcd. for $C_{21}H_{17}NS$: C, 80.0; H, 5.4. Found: C, 80.2; H, 5.5.

α-Phenyl-β-(5-β-phenylethyl-2-thienyl)acrylic acid (VII). Obtained in 55% yield by hydrolysis of the foregoing nitrile, this acid crystallized from ethanol in fine, colorless prisms, m.p. 179°.

Anal. Calcd. for $C_{21}H_{18}O_2S$: C, 75.4; H, 5.4. Found: C, 75.2; H, 5.4.

α,ω-Diphenylpelargonic acid (X). This acid, obtained in 70% yield, crystallized from methanol in fine, colorless prisms, m.p. 92°.

Anal. Calcd. for $C_{21}H_{26}O_2$: C, 81.3; H, 8.4. Found: C, 81.4; H, 8.4.

α-Phenyl-β-(5-γ-phenylpropyl-2-thienyl)acrylonitrile (V). This nitrile, prepared in 76% yield, crystallized from ethanol in shiny, yellowish leaflets, m.p. 59°.

Anal. Calcd. for $C_{22}H_{19}NS$: C, 80.2; H, 5.8. Found: C, 80.3; H, 5.9.

α-Phenyl-β-(5-γ-phenylpropyl-2-thienyl)acrylic acid (VIII). This acid (obtained in 65% yield by acid hydrolysis and in 40% yield by alkaline hydrolysis) crystallized from ethanol in fine, colorless prisms, m.p. 148°.

Anal. Calcd. for $C_{22}H_{20}O_2S$: C, 75.9; H, 5.7. Found: C, 75.7; H, 5.8.

α,ω-Diphenylcapric acid (XI). Obtained in 63% yield, this acid crystallized from methanol in shiny, colorless leaflets, m.p. 80°.

Anal. Calcd. for $C_{22}H_{28}O_2$: C, 81.5; H, 8.6. Found: C, 81.5; H, 8.8.

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Decomposition of Phenylazotriphenylmethane in the Presence of Triphenylmethyl

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Whether the thermal decomposition of unsymmetrical azoalkanes and arylazoalkanes proceeds with simultaneous cleavage of the two carbon-nitrogen bonds or with the cleavage of only one of these, followed by the other, is not known with certainty. Rampsberger,[1] considering the reactivities of azomethane, isopropylazomethane, and azoisopropane, has argued that the cleavage is of the former type, since each substitution of isopropyl for methyl results in an almost equal decrease in activation energy. Cohen and Wang[2] have argued similarly concerning the variations of activation energies among the compounds azomethane, azodiphenylmethane, azoisopropane, azo-α-phenyl-ethane, azodiphenylmethane, azoisopropane, azo-α-phenylethane, phenylazodiphenylmethane, and phenylazotriphenylmethane, but pointed out that such arguments apply only to the fragmentation of the symmetrical compounds. The latter authors suggest that reaction 1 may account for the lack of production of triphenylmethane

$$Ph—N{=}N—CHPh_2 \longrightarrow Ph—N{=}N\cdot + \cdot CHPh_2 \quad (1)$$

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(2) S. G. Cohen and C. H. Wang, *J. Am. Chem. Soc.*, **77**, 2457, 3628 (1955).