

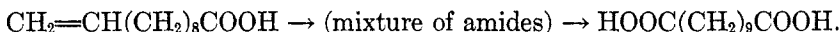
THE WILLGERODT REACTION. V. SUBSTITUTED ACETAMIDES
FROM β -SUBSTITUTED ACRYLIC ACIDS¹

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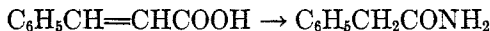
It has recently been shown that the Willgerodt reaction is not limited to use with aryl alkyl ketones but serves also for the conversion of acetylenes ($\text{RC}\equiv\text{CH}$, $\text{RC}\equiv\text{CCH}_3$) (2, 3) into carbonamides retaining the same carbon skeleton as the starting compounds ($\text{RCH}_2\text{CONH}_2$ and $\text{RCH}_2\text{CH}_2\text{CONH}_2$, respectively). Similarly, it has been demonstrated that olefins of the types $\text{RCH}=\text{CH}_2$ and $\text{RCH}=\text{CH}(\text{CH}_2)_n\text{CH}_3$ (3, 4, 5, 6), secondary carbinols of the types RCHOHCH_3 and $\text{RCHOH}(\text{CH}_2)_n\text{CH}_3$ (6), completely aliphatic ketones of the types $\text{RCO}(\text{CH}_2)_n\text{CH}_3$ (1, 6b) and mercaptans of the general structure $\text{RCHSH}(\text{CH}_2)_n\text{H}$ (6b) are converted by the action of hot ammonium polysulfide or ammonium hydroxide-sulfur mixtures into carbonamides with loss of the original functional group but with the retention of the relative arrangement of carbon atoms in the starting compound.

Undecylenic acid, the only olefinic acid previously reported (4) to have been studied under the conditions of the Willgerodt reaction, reacted normally without loss of carbon atoms and yielded a mixture of the mono- and di-amides of nonane-1,9-dicarboxylic acid, which gave pure nonane-1,9-dicarboxylic acid upon hydrolysis:

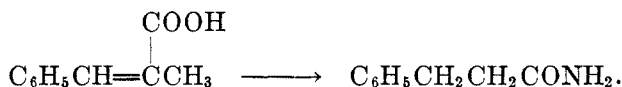


We have now extended our investigation to include α,β -unsaturated acids and have found that they react smoothly to form carbonamides having one less carbon atom than the starting acid. The carboxyl group is lost but the product otherwise retains the carbon skeleton of the original compound.

Thus, cinnamic acid gave 76.7% of phenylacetamide when it was heated with a mixture of concentrated aqueous ammonia, sulfur, and dioxane.



In the one example studied in which the aliphatic carbon chain was branched *viz.*, *trans*- α -methylcinnamic acid, the carboxyl group was eliminated from a penultimate position and the straight chain β -phenylpropionamide was formed:



This reaction suggests a close analogy to the conversion of 1-phenylpropene into β -phenylpropionamide under similar conditions (3).

¹ For previous papers of this series, see References 1-4.

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2-Nonenoic acid, chosen as an example of a completely aliphatic β -substituted acrylic acid, gave *n*-caprylamide:



The yields of amides from the acids of the type $\text{RCH}=\text{CHCOOH}$ were higher and the crude reaction products appeared to be cleaner than those obtained from the corresponding olefins ($\text{RCH}=\text{CH}_2$) in previous investigations carried out in this Laboratory (3, 4).

The interesting cleavage of 9-propionylanthracene to give a high yield of anthracene under conditions of the Willgerodt reaction (2) prompted the investigation of β -(9-anthracene)acrylic acid under similar reaction conditions. This unsaturated acid did not yield β -(9-anthracene)acetamide but, like 9-propionylanthracene, was cleaved to anthracene. The β -(9-anthracene)-acrylic acid was synthesized from 9-anthraldehyde and malonic acid by the Doebner method.

EXPERIMENTAL

Phenylacetamide from cinnamic acid. A mixture of 4.0 g. of cinnamic acid, 8.8 ml. of concentrated (15 *M*) aqueous ammonia, 5.6 g. of sulfur, and 8 ml. of dioxane was heated in a sealed glass tube at $170 \pm 5^\circ$ for five and one-half hours. When the mixture had cooled to room temperature, the supernatant liquid was decanted from the crystals of nearly pure amide, which were then washed with ammonium sulfide solution and recrystallized from water to give 1.36 g. of colorless phenylacetamide, m.p. $159\text{--}160^\circ$ cor. The mother liquor from the reaction mixture was evaporated to dryness and the remaining amide was extracted from the residue with hot water, giving an additional 1.40 g. of phenylacetamide, m.p. $158\text{--}159^\circ$; total yield, 76.7%. The identity of the product was confirmed by direct comparison with an authentic specimen.

β -Phenylpropionamide from α -methylcinnamic acid. *trans*- α -Methylcinnamic acid was prepared by the method of Perkin (7). A mixture of 4.0 g. of the *trans*- α -methylcinnamic acid, 8.8 ml. of concentrated aqueous ammonia, 5.6 g. of sulfur, and 8.0 ml. of pyridine was heated in a sealed glass tube at $170 \pm 5^\circ$ for five and one-half hours. The reaction mixture was evaporated to dryness and the product extracted thoroughly with hot water. From the clarified extracts β -phenylpropionamide separated as colorless needles, yield, 2.31 g. (63%), m.p. $98\text{--}99^\circ$ cor. One recrystallization from water (Norit) yielded 2.00 g., m.p. $101\text{--}102^\circ$ cor., not depressed by admixture with an authentic specimen of β -phenylpropionamide (m.p. $100\text{--}101.5^\circ$).

n-Caprylamide from 2-nonenoic acid. 2-Nonenoic acid was prepared according to the procedure of Zaar (8). A mixture of 4.0 g. of 2-nonenoic acid, 8.8 ml. of concentrated aqueous ammonia, 5.6 g. of sulfur, and 8.0 ml. of pyridine was heated in a sealed glass tube at $160 \pm 5^\circ$ for four and one-half hours. The contents of the tube were evaporated to dryness and extracted with ether to remove the amide. The dark, waxy solid from the ether was recrystallized from 50% alcohol (Norit) to give 2.46 g. (69%) of slightly impure amide. A second recrystallization from 50% alcohol gave 1.49 g. (41%), m.p. $102.5\text{--}103.5^\circ$. After another recrystallization, from ligroin, the amide was obtained as 1.23 g. of shining plates, m.p. $104\text{--}105^\circ$ cor.; the melting point has been reported as 105° (9) and 106° (10). The amide was hydrolyzed to the acid in boiling glacial acetic acid-hydrochloric acid, and the acid was converted into the anilide, which melted, after recrystallization from 50% alcohol, at $51.5\text{--}52^\circ$; the reported m.p. is 55° (9).

β -(9-Anthracene)acrylic acid. A mixture of 2.06 g. of 9-anthraldehyde (11, 12), 1.4 g. of malonic acid, 0.5 ml. of piperidine, and 3.0 ml. of pyridine was heated on the steam-bath

for four hours; the solution was then refluxed for one hour in an oil-bath at 125–130°. The mixture was cooled, diluted with 20 ml. of water, and acidified with dilute hydrochloric acid. The orange oil which separated soon solidified. The orange solid weighed 3.08 g. when dry and began to melt with decomposition at about 145°; it evidently consisted largely of the substituted malonic acid. The material was heated for thirty minutes at 180–190° to eliminate carbon dioxide. The dark red melt solidified on cooling and was purified by recrystallization from 12 ml. of chlorobenzene containing 0.5 ml. of glacial acetic acid. β -(9-Anthracene)acrylic acid formed bright yellow needles, m.p. 235.5–237.5° (dec.); yield, 2.05 g. (82.6%). A second recrystallization gave a first crop of 1.80 g., m.p. 246–247° (dec.). The analytical sample was recrystallized once from acetone-ethyl acetate.

Anal. Calc'd for $C_{17}H_{12}O_2$: C, 82.24; H, 4.87.

Found³: C, 82.12; H, 4.96.

Cleavage of β -(9-anthracene)acrylic acid under Willgerodt conditions. A mixture of 0.60 g. of β -(9-anthracene)acrylic acid, 1.3 ml. of concentrated aqueous ammonia, 0.84 g. of sulfur, and 1.2 ml. of dioxane was heated in a sealed glass tube at $170 \pm 5^\circ$ for five and one-half hours. The reaction mixture was evaporated to dryness and the dry residue extracted with boiling glacial acetic acid. The only crystalline material isolated from the acetic acid after clarification with Norit was anthracene in 50% yield. The anthracene, after recrystallization from chlorobenzene, consisted of yellow plates, m.p. 215–216° cor.; the melting point was not depressed by admixture with pure anthracene, m.p. 216–217° cor.

SUMMARY

Cinnamic acid gave phenylacetamide under the conditions of the Willgerodt reaction. *trans*- α -Methylcinnamic acid yielded β -phenylpropionamide, and 2-nonenic acid yielded *n*-caprylamide. β -(9-Anthracene)acrylic acid was cleaved to anthracene in a manner similar to 9-propionylantracene.

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³ Analysis by Mr. John F. Dowdall.