Studies in the Propiothiolactone Series. IV. Reaction of 
β-Benzylmercaptocrotopropionyl Chloride with Benzene in the 
Presence of Aluminum Bromide

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Continuing the studies of the effect of the α-substituent 
upon the course of the Friedel-Crafts reaction the behaviour of 
α-unsubstituted β-benzylmercaptocrotopropionyl chloride was descri­ 
based. When one or two moles of aluminum bromide was used, the 
main products were β-mercaptocrotopropene and β-benzylmer­
 captocrotopropene. Diphenylmethane was isolated in about 90% yield. With three moles of aluminum bromide the main product 
obtained from the reaction mixture was β-mercaptocrotopropene 
and no β-benzylmercaptocrotopropene could be isolated. The crude 
products from the reaction with three moles of aluminum bromide 
gave a high yield of 3,3'-thiodiprotopropene when treated with 
aqueous ammonia at room temperature.

The nature of the products obtained from the reaction of α-acylamino­
-β-benzylmercaptocrotopropionyl chloride with aluminum halides in benzene was 
described in previous papers by D. Fleš et al.1 and was found to be dependent 
upon the amount of aluminum halide. Thus, α-phthalimido-β-benzylmercap­
tocrotopropionyl chloride treated with one mole of aluminum chloride gave a polythio­
ester (I), while with two moles of aluminum chloride propiothiolactone (II) was 

![Chemical Structure](I)

Using the same reaction conditions with two moles of aluminum chloride, 
α-succinimido and α-p-toluenesulfonamido-β-benzylmercaptocrotopropionyl chloride 
were converted to the corresponding propiothiolactones².

In no case was the corresponding propiophenone isolated, which indicates 
that in these reactions debenzylation is a more rapid process than acylation. 
The debenzylation was followed by inter- or intramolecular esterification to 
yield either polythioester or propiothiolactone.

Continuing the studies of the effect of the α-substituent upon the course of the Friedel-Crafts reaction the behaviour of α-unsubstituted β-benzylmercaptocaproyl chloride treated with variable amounts of aluminum bromide in benzene at room temperature was described. Aluminum bromide was used because of its solubility in benzene.

When one or two moles of aluminum bromide was used, the main products were β-mercaptocaproylphenone (III) and β-benzylmercaptocaproylphenone (IV).

\[
\text{HSCH}_2\text{CH}_2\text{COC}_6\text{H}_5 \quad \text{C}_9\text{H}_6\text{SCH}_2\text{CH}_2\text{CH}_2\text{COC}_6\text{H}_5
\]

III IV

Diphenylmethane was isolated in about 90% yield.

Ketones III and IV were separated by fractional distillation and identified by conversion to propiophenone. β-Mercaptocaproylphenone was converted directly to propiophenone by desulfuration with Raney nickel, while β-benzylmercaptocaproylphenone was first debenzylated with aluminum bromide in benzene to yield diphenylmethane and β-mercaptocaproylphenone, which was subsequently desulfurized to propiophenone.

With three moles of aluminum bromide the main product obtained from the reaction mixture was β-mercaptocaproylphenone; no β-benzylmercaptocaproylphenone could be isolated. It is noteworthy that a large amount of hydrogen sulfide was evolved during the hydrolysis of the aluminum bromide.

The crude reaction products gave a high yield of 3,3'-thiodipropiophenone when treated with aqueous ammonia at room temperature. The reaction mixture obtained with one or two moles of aluminum bromide gave no 3,3'-thiodipropiophenone when treated with ammonia under the same conditions.

Summarizing the experimental results, it may be concluded that in the reaction of β-benzylmercaptocaproyl chloride with benzene under conditions of a Friedel-Crafts reaction, the ketone formation is faster than the debenzylation reaction. Consequently propiophenone derivatives are formed easier than propiothiolactones or polythioesters, which resulted when propionylchloride was substituted in the α-position.

**EXPERIMENTAL**

All melting points are uncorrected.

**β-Benzylmercaptocaproyl acid**

β-Benzylmercaptocaproyl acid (11.0 g., 56%), m.p. 82° (recrystallized from benzene-petroleum ether) (lit. 3: m.p. 82°) was prepared from β-bromopropionic acid (15.3 g., 0.1 mole) following the method of Stoner and Hougherty 4 for benzylmercaptoacetic acid.

\[
\text{Anal. C}_{10}\text{H}_{12}\text{O}_{2}\text{S} \quad (196.27) \quad \text{calc'd.: C 61.19; H 6.16/}\%
\]

\[
\text{found : C 61.01; H 6.32/}\%
\]

**Reaction of β-benzylmercaptocaproyl chloride with benzene in the presence of two moles of aluminum bromide**

To a solution of 43.1 g. (1.64 moles) of anhydrous aluminum bromide in 250 ml of dry benzene was added at once a solution of 17.5 g. (0.82 moles) of β-benzylmercaptocaproyl chloride 5 in 50 ml. of dry benzene. The reaction mixture was
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vigorously stirred for one hour at room temperature and then hydrolyzed with 200 g. of ice and 40 ml. of concentrated hydrochloric acid. The water layer was separated and extracted with three 80-ml. portions of benzene, the combined benzene layers were washed with three 50-ml. portions of dilute aqueous sodium bicarbonate and dried over sodium sulfate. Benzene was removed under reduced pressure yielding 20.0 g. of an oily residue. The crude oily product was refluxed for one hour with 16.0 g. of Girard T reagent in 184 ml. of absolute ethanol and 16 ml. of glacial acetic acid. The reaction mixture was poured into 400 g. of ice containing 25.6 g. of anhydrous sodium carbonate. The resulting mixture was extracted with three 100-ml. portions of ether, the ethereal extracts dried over sodium sulfate and evaporated in vacuo to give 12.2 g. (89.1%) of diphenylmethane which was purified by distillation at 95—100° and 0.2 mm.³

Anal. C₁₃H₁₂ (168.23) calc'd.: C 92.85; H 7.15%
found: C 92.70; H 7.10%

To the water layer from which diphenylmethane was extracted was added 24 ml. of concentrated hydrochloric acid and the reaction mixture left at room temperature for one hour. The crude ketonic material was taken into five 100-ml. portions of benzene. The benzene extract was washed with three 50-ml. portions of water and dried over sodium sulfate. Benzene was evaporated in vacuo to give 7.7 g. (57% calculated on basis of the conversion of β-benzylmercaptocaproproplonyl chloride to β-mercaptocaptopropiophenone) of an oily residue. Crude oil was distilled at 0.05 mm and fractionated into two distinct fractions: one boiling at 215—290 (5.1 g., 37.7% based on β-benzylmercaptocaproproplonyl chloride) and the other boiling at 235—400 (0.5 g., 3% based on acid chloride).

The first fraction was identified as β-mercaptocaptopropiophenone (III).

Anal. C₉H₁₀O₅ (256.36) calc'd.: C 74.96; H 6.29%
found: C 74.69; H 6.15%

A sample of β-benzylmercaptocaptopropiophenone prepared following the method of Böhme and Heller was identical with the compound IV as indicated by its boiling points and IR spectra.

Desulfuration of β-mercaptocaptopropiophenone

β-Mercaptocaptopropiophenone (0.5 g., 0.003 moles) was dissolved in 10 ml. of benzene and 2 g. of Raney nickel C in 50 ml. of absolute ethanol was added. The reaction mixture was heated under reflux with vigorous stirring for five hours and left overnight at room temperature. Nickel was removed by filtration, washed with two 15-ml. portions of absolute ethanol and the combined filtrate and washings were evaporated in vacuo to give 0.4 g. of an oily product. The crude oil was extracted with 5 ml. of hot absolute ethanol and treated with 0.5 g. of a methanolic solution of 2,4-dinitrophenylhydrazine. After standing overnight at room temperature a crystalline product precipitated. Yield 0.3 g. The analytical sample of propiophenone-2,4-dinitrophenylhydrazone was crystallized from dry benzene, m.p. 193—40, undepressed with an authentic sample.¹⁰

Debenzylation of β-benzylmercaptocaptopropiophenone

β-Benzylmercaptocaptopropiophenone (0.5 g., 0.002 moles) in 10 ml. of dry benzene was stirred with a solution of 1.5 g. (0.006 moles) of aluminum bromide in 20 ml. of dry benzene at room temperature for two hours. After hydrolysis of the reaction product with 10 g. of ice in 1.5 ml. of concentrated hydrochloric acid, the water layer was extracted with three 15-ml. portions of benzene, the combined benzene
layers washed with dilute aqueous sodium bicarbonate and dried over sodium sulfate. Benzene was evaporated in vacuo to give 0.5 g. of an oily product. Extraction with three 20-ml. portions of petroleum ether yielded upon evaporation of solvent 0.3 g. of diphenylmethane.

The oily residue after extraction of diphenylmethane was desulfurized with Raney nickel C and the remaining oil (0.2 g.) converted with a methanolic solution of 2,4-dinitrophenylhydrazine to propiophenone-2,4-dinitrophenylhydrazone, m.p. 193—4°, undepressed with an authentic sample.

**Reaction of β-benzylmercaptopropionyl chloride with benzene in the presence of three moles of aluminum bromide**

A solution of β-benzylmercaptopropionyl chloride (5.0 g., 0.02 moles) in 20 ml. of benzene was treated with 20.0 g. of aluminum bromide (0.07 moles) in 100 ml. of dry benzene as previously described. On hydrolysis with ice and hydrochloric acid a strong evolution of hydrogen sulfide occurred. After evaporation of the benzene layer, 5.2 g. of an oily product was obtained. By extraction with petroleum ether in the previously described manner, diphenylmethane (3.4 g., 87/o) was isolated.

The oily residue (1.5 g.) obtained after extraction of diphenylmethane was chromatographed on neutral aluminum oxide and eluted with dry benzene. After evaporation of benzene, 1.3 g. of an oily product was obtained. A sample was distilled for analysis at 220—5° and 0.05 mm. IR absorption spectrum was identical with that of ß-mercaptopropiophenone.

**3,3'-Thiodipropiophenone**

To 1.0 g. of the crude oily product of the reaction of ß-benzylmercaptopropionyl chloride with benzene in the presence of three moles of aluminum bromide was added 20 ml. of aqueous ammonia. After standing for 10 days at room temperature 0.7 g. of diphenylmethane was extracted with petroleum ether and the residue recrystallized from ethanol to give white crystals (0.2 g.), m.p. 104—5°, reported 104° 11.

**REFERENCES**

7. K. V. Auwers and A. Frühling, Ann. 422 (1921) 221.
IZVOD

Studije u redu propiotiolaktona. IV. Reakcija β-benzilmerkaptopropionil klorida s benzenom u prisutnosti aluminijeva bromida

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U nastavku ispitivanja utjecaja α-supstituenta na tok Friedel-Crafts-ove reakcije izvedena je reakcija β-benzilmerkaptopropionil klorida sa različitim količinama aluminijskog bromida u benzenu na sobnoj temperaturi. Upotrebom jednog ili dva mola aluminijskoga bromida dobiveni su kao glavni reakcioni produkti β-merkaptopropiofenon i β-benzilmerkaptopropiofenon, a difenilmetan je izoliran u iskorištenju od oko 90%. Sa tri mola aluminijskog bromida nastao je kao glavni produkt reakcije β-merkaptopropiofenon, dok β-benzilmerkaptopropiofenon nije izoliran. Sirovi produkti reakcije u prisutnosti tri mola aluminijskog bromida dali su obrađom sa amonijakom visoko iskorištenje 3,3'-tiodipropiofenona.

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