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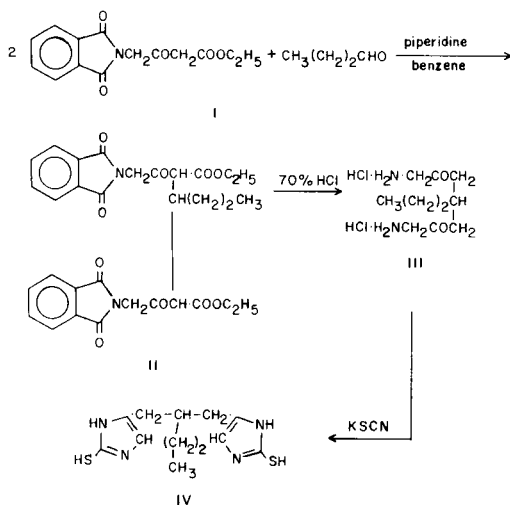
Ethyl butylidene-*bis*-3-phthalimidoacetoacetate (II) was prepared by condensation of ethyl-3-phthalimidoacetoacetate and *n*-butyraldehyde in the presence of piperidine in benzene. Compound II was hydrolysed by hydrochloric acid followed by cyclization with potassium thiocyanate to yield *bis*-(2-mercaptoimidazole)-4,4-butyldiene (IV).

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Imidazoles and derivatives thereof are well known for their biological activities. It was therefore thought to be worthwhile to extend our previous work (2) on such derivatives. While studying the Knoevenagel reaction between *n*-butyraldehyde and ethyl 3-phthalimidoacetoacetate (I) in the presence of piperidine using sodium dried benzene as a solvent, a side product was isolated in 7% yield. This product has been identified and assigned the structure II based on elemental and spectral studies.

The present communication deals with the synthesis of II by the condensation of 2 moles of I with one mole of *n*-butyraldehyde in the presence of piperidine using sodium dried benzene as a solvent. Compound II was hydrolysed with 70% hydrochloric acid giving the dihydrochloride of 1,7-diamino-4-propylheptane-2,6-dione (III). Cyclization with potassium thiocyanate yielded *bis*-(2-mercaptoimidazole)-4,4-butyldiene (IV).

Thus, a new route for the synthesis of ethyl alkylidene *bis*-3-phthalimidoacetoacetate and its utilization for the preparation of *bis*-(2-mercaptoimidazole)-4,4-alkylidene has been achieved in excellent yields. The course of the reaction may be represented as shown below.



## EXPERIMENTAL

Preparation of Ethyl Butylidene-*bis*-3-phthalimidoacetoacetate (II).

Phthalimidoacetoacetic ester (11.0 g., 0.04 mole) and 1.44 g. (0.02 mole) of *n*-butyraldehyde in 150 ml. of sodium dried benzene in the presence of 30 drops of piperidine were allowed to react in a 250 ml. round bottom flask for 48 hours in an ice box. After allowing the mixture to stand at room temperature for 24 hours, the flask was set for downward distillation and the benzene was distilled. The remaining residue was extracted with 50 ml. of hot absolute alcohol and the whole was kept at room temperature for 18 hours. The resulting colourless crystals of II in petal like bunches were filtered and vacuum dried (m.p. 114° sharp, yield 51%). The product is soluble in benzene, chloroform, absolute alcohol, dimethylformamide, ethylacetate and acetone, and insoluble in ether and water. It was recrystallized from absolute alcohol. The ir spectrum of II showed absorption bands at 1730  $\text{cm}^{-1}$  ( $> \text{C} = \text{O}$ ), 1750  $\text{cm}^{-1}$  ( $> \text{C} = \text{O}$  of ester group), 1635  $\text{cm}^{-1}$  ( $\text{C} = \text{C}$ ) and 1655  $\text{cm}^{-1}$ , indicating the presence of an ester carbonyl group after chelation to the enolic hydroxyl group.

*Anal.* Calcd. for  $\text{C}_{32}\text{H}_{32}\text{N}_2\text{O}_{10}$ : C, 63.57; H, 5.29; N, 4.63. Found: C, 63.48; H, 5.22; N, 4.60.

Preparation of *Bis*-(2-mercaptoimidazole)-4,4-butyldiene (IV).

Compound II (10 g.) was heated with 75% hydrochloric acid (200 ml.) for 3 hours until the ester dissolved. On cooling most of the phthalic acid separated and was filtered. The filtrate was concentrated to half the volume on a water bath, and then chilled in ice. The precipitated phthalic acid was again filtered and the filtrate was evaporated to dryness under reduced pressure. The highly hygroscopic dihydrochloride of 1,7-diamino-4-propylheptane-2,6-dione (III) crystallized as light yellow needles (m.p. 99.5°, yield 59%).

Compound III was dissolved in ethanol and precipitated with ether. The precipitate was quickly filtered and dissolved in 15 ml. of water. Potassium thiocyanate (2.25 g.) dissolved in 5 ml. of water, was then added and the mixture was heated on a water bath for 3 hours followed by evaporation to dryness. The residue was dissolved in warm water (80 ml.) and treated with a saturated solution of mercuric acetate until the precipitation was complete. The light yellow precipitate of the mercury complex of IV was suspended in water (40 ml.), made acidic with dilute hydrochloric acid, and hydrogen sulfide gas was passed through the mixture. The mercury sulphide was filtered and washed twice with 15 ml. portions of water. The combined filtrate and washings were treated with charcoal and filtered. The clean filtrate was evaporated to dryness when the dihydrochloride of IV was obtained as a yellowish white, hygroscopic needles (m.p. 275°, yield 56%). This product was dissolved in dry ethanol and neutralized with ethanolic sodium hydroxide, and the precipitated sodium chloride was filtered. Evaporation to crystallization gave pure IV, m.p. 260° dec., yield 51%. The presence of the characteristic band of the  $\text{C}=\text{N}$  (1605  $\text{cm}^{-1}$ ) group in the ir spectrum of IV provided further

support for the structure of the product.

*Anal.* Calcd. for  $C_{12}H_{18}N_4S_2$ : N, 19.85; S, 22.69. Found: N, 19.81; S, 22.60.

Acknowledgement.

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#### REFERENCES AND NOTES

- (1) Presented at the Seventh International Congress of Heterocyclic Chemistry, 1979.
- (2) Ashutosh, N. D. Pandey and J. K. Mehrotra, *Heterocycles*, **12**, 1339 (1979).