pression of the melting point when mixed with an authentic specimen.

Physical Measurements.—For the determination of solubilities an excess of the acid was placed in a glass-stoppered graduated cylinder to which a known volume of solvent had been added. The mixture was placed in a thermostatically controlled water-bath at 25 ± 0.05° and left for several hours, shaking periodically. Filtered samples were titrated with standard sodium hydroxide to thymolphthalein.

Densities were determined with Reischauer pyknometers and refractive indices with a Bausch and Lomb Abbe refractometer which had been calibrated at the D line with Bureau of Standards certified test prisms.

Melting points were determined with the aid of a carefully calibrated Dennis–Parr melting point bar. Temperatures were measured thermoelectrically using a special Leeds and Northrup portable potentiometer reading directly in degrees centigrade for copper–constantan thermocouples and graduated in units of 0.5°.

Summary

1. Eight 5-alkyl-5-β-hydroxyethyl-2-thiobarbituric acids have been prepared by the condensation of α-alkyl-α-carboxethyl-γ-butyric lactones with thiourea in the presence of sodium ethoxide.

2. High yields were obtained using molar ratios of sodium, thiourea and lactone of 2:1·5:1, respectively, at maximum temperatures of 35°. These conditions are considerably less drastic than those for the synthesis of the corresponding barbiturates.

3. In two cases the intermediate lactone thioureides have been isolated.

4. A molecular compound of the sodium *n*-butylthiobarbiturate with sodium ethoxide was obtained.

5. A rapid and simple method for the estimation of conversion is illustrated and a new technique by which six of the eight thiobarbituric acids can be recovered nearly quantitatively is described.

6. Physical properties studied include melting points and solubility in common solvents.

7. Modifications of existing methods of preparation and physical properties of the intermediates are discussed. These include alkylmalonic esters and α-alkyl-α-carboxethyl-γ-butyric lactones.

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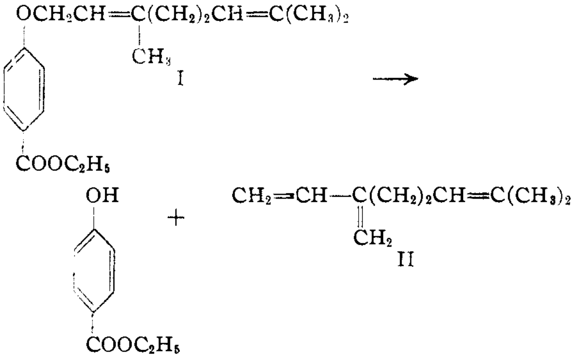
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

The Pyrolysis of Ethyl *p*-Geranyloxybenzoate[1]

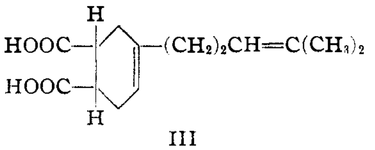
BY WALTER M. LAUER AND RAFAEL LABRIOLA[2]

The pyrolysis of only a few γ,γ-disubstituted allyl phenyl ethers has been studied. Claisen reported, but without experimental detail, that the pyrolysis of γ,γ-dimethylallyl phenyl ether yields isoprene and phenol[3] and Hurd and Cohen[4] showed that α,α,γ,γ-tetramethylallyl phenyl ether likewise gave cleavage products, in this case hexadiene and phenol. Lauer and Moe[5] studied the pyrolysis of ethyl *p*-(γ,γ-dimethylallyloxy)-benzoate; the cleavage products, isoprene and ethyl *p*-hydroxybenzoate were obtained together with 2,2,3-trimethylcoumaran. The formation of 2,2,3-trimethylcoumaran was accounted for on the basis of an abnormal rearrangement followed by ring closure. The geranyl, farnesyl and phytyl radicals are γ,γ-disubstituted allyl radicals. In view of their importance in the field of natural products, it was considered of interest to extend the aforementioned pyrolysis studies to the next higher isoprenolog, ethyl *p*-geranyloxybenzoate.

The results of the present study show that pyrolysis of ethyl *p*-geranyloxybenzoate (I) at temperatures approximating 200° yields the unsaturated hydrocarbon myrcene (II) and ethyl *p*-hydroxybenzoate. There was no evidence indicating the formation of either an abnormal or normal rearrangement product; consequently the behavior of this ester on heating is represented by the equation



The unsaturated hydrocarbon produced in this pyrolysis formed an addition product with maleic anhydride. The dibasic acid III, prepared by hydrolysis of this addition product, melted at the temperature reported by Diels and Alder.



III

Experimental

Geranyl bromide (b. p. 109° at 20 mm.; n^{15}D 1.5005) was prepared from geraniol (b. p. 104–110° at 9 mm.;

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[1] Paper X in series on the Phenyl Allyl Ethers.

[2] Professor of Organic Chemistry, The University of Buenos Aires, Argentina, and Fellow of the Guggenheim Foundation.

[3] Claisen and Tietze, *Ber.*, **59B**, 2344 (1926).

[4] Hurd and Cohen, THIS JOURNAL, **53**, 1917 (1931).

[5] Lauer and Moe, *ibid.*, **65**, 291 (1943).

$n^{22}\mathrm{D}$ 1.4710), pyridine and phosphorus tribromide according to the procedure of Schmitt.[6]

Ethyl *p*-Geranyloxybenzoate.—Ethyl *p*-hydroxybenzoate (16.6 g., 0.1 mole), dissolved in acetone (50 ml.), was placed in a three-necked flask fitted with a reflux condenser, a dropping funnel and a motor-driven stirrer. Anhydrous potassium carbonate (14 g., 0.1 mole) was then added and while the mixture was stirred, geranyl bromide (22 g., 0.1 mole) was dropped into the reaction mixture. After heating under reflux for six hours, the reaction mixture was cooled and filtered; most of the acetone was then removed by distillation and the solid salts were dissolved in water. The oil which separated was collected and the aqueous solution was extracted repeatedly with ether. The ether extracts combined with the oil were washed with aqueous (10%) sodium hydroxide and finally with water. The ether solution yielded the crude ester (16.3 g.), and ethyl *p*-hydroxybenzoate (6.2 g.), one of the starting materials was recovered from the alkaline extract.

The crude ethyl *p*-geranyloxybenzoate (16.0 g.) was hydrolyzed in boiling methanolic potassium hydroxide. After the major portion of methanol was removed, water was added and the aqueous solution was extracted with ether. Acidification of the aqueous solution precipitated the crude acid (10 g.). Crystallization from a benzene–ligroin mixture yielded the pure acid, *p*-geranyloxybenzoic acid (m. p. 113–114°).

Anal. Calcd. for $C_{17}H_{22}O_3$: C, 74.45; H, 8.02. Found: C, 74.65; H, 8.23.

The **silver salt** of this acid was prepared as follows: *p*-Geranyloxybenzoic acid (21 g.) was suspended in water and the calculated amount of sodium bicarbonate (6.6 g.) was added to bring the acid into solution. The addition of silver nitrate precipitated the silver salt (26 g.).

The silver salt was then suspended in dry ether and an excess of ethyl iodide was added to the stirred reaction mixture. Boiling was continued for four to five hours, after which the ether solution was filtered to remove the silver iodide. Ethyl *p*-geranyloxybenzoate was isolated from the ether solution by distillation under reduced pressure (0.1 mm., bath temp. 150–160°). The ester was not redistilled, since it was considered inadvisable to subject it to further heating before investigating its behavior on pyrolysis.

Anal. Calcd. for $C_{19}H_{26}O_3$: C, 75.48; H, 8.61. Found: C, 74.84; H, 8.72.

Pyrolysis.—The ethyl ester (7.5 g.) was heated (metal bath, 200°) to boiling (2.5 hrs.) under reduced pressure (30 mm.). Provision was made (Dry Ice trap) for the collection of volatile products. Myrcene (1.7 g.) was obtained as one of the pyrolysis products. A determination of the boiling point (61–62° at 14 mm.; reported 63–65° at 14 mm.) and refractive index ($n^{21}\mathrm{D}$ 1.4705; reported $n^{20}\mathrm{D}$ 1.470), together with the preparation of the dibasic acid (m. p. 122°; reported by Diels and Alder,[7] 122–123°) obtained by the hydrolysis of the maleic anhydride addition product served to characterize the myrcene.

The solid pyrolysis product was dissolved in ether and the ether solution was extracted with aqueous alkali and finally with Claisen alkali. The alkali-soluble portion upon acidification yielded ethyl *p*-hydroxybenzoate (m. p. and mixed m. p. 117–118°; 3.0 g.). The ether solution after this extraction with alkali contained an oil (2.3 g.) which was subjected to the action of methanolic potassium hydroxide. Acidification gave a low-melting solid, which was difficult to purify; consequently it was hydrogenated in ethanol using a platinum oxide catalyst. A wax-like product was obtained. The *p*-bromophenacyl ester of this wax-like substance was prepared. This ester (m. p. 93–94°) proved to be identical with the corresponding compound prepared from the synthetic perhydrogeranyl ether.

Anal. Calcd. for $C_{25}H_{29}O_4Br$: C, 63.42; H, 6.13. Found: C, 63.34; H, 6.34.

***p*-Perhydrogeranyloxybenzoic acid.**—Perhydrogeraniol, obtained by the catalytic reduction of geraniol, was converted to the bromide according to the procedure of Smith, *et al.*[8] Ethyl *p*-hydroxybenzoate (16.6 g.) dissolved in acetone (60 ml.), was placed in a three-necked flask fitted with a reflux condenser, dropping funnel and stirrer. Anhydrous potassium carbonate (14 g.) was then added, after which perhydrogeranyl bromide (22 g.) was dropped into the reaction mixture. Heating under reflux was continued for six hours, after which most of the acetone was removed from the reaction mixture by distillation. Water was then added and the aqueous solution was extracted with ether. The ether extract, after washing with aqueous sodium hydroxide, yielded the crude ester (24 g.). Hydrolysis was accomplished by boiling with methanolic potassium hydroxide for several hours. Most of the methanol was then removed and water was added. The aqueous solution after extraction with ether, was acidified with hydrochloric acid. The acid (14 g., m. p. 96°) was crystallized from ethanol.

Anal. Calcd. for $C_{17}H_{26}O_3$: C, 73.74; H, 9.35. Found: C, 73.78; H, 9.60.

The **hydrogenation of *p*-geranyloxybenzoic acid** was carried out in the presence of alcohol and platinum oxide. After removal of the catalyst and the ethanol, the reduction product was crystallized from methanol. A product melting at 95° was obtained. A mixed melting point with the substituted acid obtained from perhydrogeranyl bromide was also 95°.

The *p*-bromophenacyl ester (m. p. 93°) of *p*-perhydrogeranyloxybenzoic acid was prepared in the customary manner.

Summary

Ethyl *p*-geranyloxybenzoate, a γ,γ-disubstituted allyl phenyl ether, was subjected to pyrolysis. The cleavage products myrcene and ethyl *p*-hydroxybenzoate were obtained, and there was no evidence of the formation of either normal or abnormal rearrangement products.

MINNEAPOLIS, MINNESOTA RECEIVED MAY 21, 1945

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[6] Josef Schmitt, *Ann.*, **547**, 119 (1941).

[7] Diels and Alder, *ibid.*, **470**, 81 (1929).

[8] Smith, Austin, Ungnade, Prichard and Opie, *J. Org. Chem.*, **4**, 338 (1939); Natelson, Gottfried and Kornblau, THIS JOURNAL, **64**, 1484 (1942).