[Contribution from the Department of Organic Chemistry, Radium Institute, University of Paris]

Arylation of Esters of Erucic Acid

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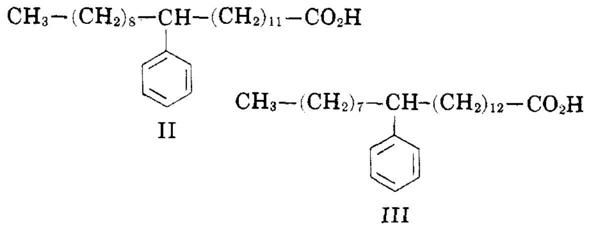
The double bond in the molecule of alkyl erucates is shown to undergo aluminum chloride-catalyzed arylation with various aromatics, and the properties of the resulting alkyl arylbehenates are investigated. Several high molecular ketones derived from erucic and behenic acid are described.

The aluminum chloride-catalyzed addition of aromatic hydrocarbons to the double bond of oleic acid and its esters has frequently been investigated[1] in connection with the manufacture of lubricants and of catalysts for hydrolysis of fats (Twitchell reagents). During World War II, in view of the critical shortage of petroleum products in France, this reaction was extensively studied by the senior author of this paper, in relation to the production of alkyl arylstearates as a substitute for spindle oils, and of arylated oleic acid glycerides for use as lubricants with high viscosity indices. Esters and glycerides of erucic acid (I) (*e.g.*, rape seed oil), which were found less satisfactory for this purpose than oleic acid derivatives, did not acquire any practical interest, but some results obtained during this research are now recorded for chemical information.

Ethyl erucate readily condensed with benzene in the presence of aluminum chloride to give a liquid ethyl phenylbehenate, which was probably a mixture of at least two isomers, the ethyl esters of 13-phenylbehenic acid (II) and of 14-phenylbehenic acid (III), and possibly of still further isomers resulting from a shift of the double bond during arylation. Such a displacement is known to occur with ethyl oleate, as the "phenylstearic acid" obtained on saponification has melting points considerably lower than any mixture of 9- and 10-phenylstearic acid, and cannot be resolved into any pure solid isomer. With ethyl phenylbehenate, however, the semi-solid complex mixture of phenylbehenic acids obtained on saponification afforded one solid isomer, of undetermined constitution. Arylation of ethyl erucate with toluene gave similar results, the ethyl *p*-tolylbehenate obtained being converted by saponification into a waxy mixture from which one solid *p*-tolylbehenic acid could be isolated by crystallization. On the other hand, arylation of methyl or ethyl erucate with ethylbenzene, diphenyl, anisole, and veratrole yielded alkyl arylbehenates from which no individual arylbehenic acid could be obtained.

$$CH_3-(CH_2)_7-CH{=}CH-(CH_2)_{11}-CO_2H$$

I



$$CH_3-(CH_2)_8-\underset{C_6H_5}{CH}-(CH_2)_{11}-CO_2H$$

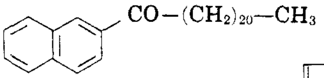
II

$$CH_3-(CH_2)_7-\underset{C_6H_5}{CH}-(CH_2)_{12}-CO_2H$$

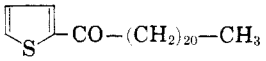
III

Throughout this study it was observed that the double bond in the molecule of erucic acid was far less susceptible to arylation than that of oleic acid. In all the experiments, a high proportion of the alkyl erucate was recovered unchanged, and there was little evidence of the fixation of two or more molecules of alkyl erucate on one molecule of the aromatic, in contrast with what had been observed with esters of oleic acid.[2] This was unfortunate, since this polyfixation process leads to oils with high viscosity indices which are of value as lubricant dopes.

Alkyl aryl ketones derived from higher fatty acids have also been frequently prepared and investigated as possible intermediates for the oil and wax industry,[3] and some new high molecular ketones of this type have now been synthesized from erucic and behenic acid. The Friedel-Crafts condensation of behenoyl chloride with naphthalene in nitrobenzene afforded 2-behenonaphthone (IV); a stannic chloride-catalyzed condensation of the same chloride with thiophene yielded 2-behenothienone (V), and 2-erucothienone (VI) was similarly obtained from erucic acid chloride. Ketones bearing methoxy groups, such as 1-methoxy-2-behenonaphthone (VII) and 2-methoxy-5-methylbehenophenone, were prepared by methylation of the



IV



V

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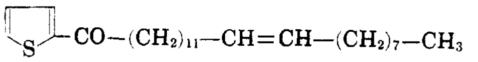
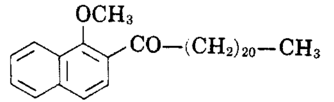
[1] *Cf.* Ben Nicolet and De Milt, *J. Am. Chem. Soc.*, **49**, 1103 (1927); Stirton and Peterson, *Ind. Eng. Chem.*, **31**, 856 (1939); Buu-Hoï and Xuong, *Bull. soc. chim.*, **15**, 751 (1948); Xuong and Buu-Hoï, *Chimie & industrie*, **63**, 507 (1950).

[2] Buu-Hoï and Cagniant, *Bull. soc. chim.*, **10**, 483 (1943).

[3] *Cf.* Ralston, Christensen, and Bauer, U.S. Patent 2,033,545 (10 March 1936); Mikeska and Cohen, *J. Org. Chem.*, **6**, 787 (1941); Buu-Hoï and Cagniant, *Bull. soc. chim.*, [5] **9**, 104 (1942).



VI



VII

readily accessible corresponding hydroxy ketones.[4]

Acknowledgment. We are indebted to the Compagnie Française de Raffinage for a subsidy to our Laboratory during the years 1940–1942.

EXPERIMENTAL

Addition of benzene to ethyl erucate. To a mixture of 92 g. of ethyl erucate and 50 g. of dry benzene, 55 g. of finely powdered aluminum chloride was added portionwise at room temperature, with stirring. The dark brown mixture was kept for two hours with frequent shaking, then poured on ice; the organic layer was taken up in benzene, and the benzene solution was washed with aqueous sodium carbonate, then with water, and dried over sodium sulfate. After evaporation of the solvent, the residue was vacuum-distilled, giving 37 g. (33%) of *ethyl phenylbehenate,* pale yellow odorless oil, b.p. 233–235°/0.3 mm., n_D^{25} 1.4657.

Anal. Calc'd for $C_{30}H_{52}O_2$: C, 81.1; H, 11.7. Found: C, 81.0; H, 11.8.

x-Phenylbehenic acid. Ethyl phenylbehenate (25 g) was refluxed for one hour with a solution of 6.2 g. of potassium hydroxide in ethanol (50 ml.), the solvent was removed by vacuum-distillation, and the residue was treated with dilute hydrochloric acid and benzene. The benzene solution was washed with water and then was dried over sodium sulfate, and the solvent was removed. Yield, 18 g. of a viscous oil which after a long period in the refrigerator deposited a crystalline mass. This was filtered off, and recrystallized from light petroleum to give waxy colorless leaflets, m.p. 48°. Yield, 2 g.

Anal. Calc'd for $C_{28}H_{48}O_2$: C, 80.8; H, 11.5. Found: C, 80.6; H, 11.8.

Marcusson[5] mentioned a phenylbehenic acid which he obtained from erucic acid and benzene, without giving details.

Addition of toluene to ethyl erucate. A similar reaction performed with 92 g. of ethyl erucate and 50 g. of dry toluene in the presence of 55 g. of aluminum chloride, afforded 35 g. (30% yield) of *ethyl tolylbehenate,* a pale yellow oil, b.p. 245–248°/0.5 mm., n_D^{26} 1.4832.

Anal. Calc'd for $C_{31}H_{54}O_2$: C, 81.0; H, 11.7. Found: C, 81.1; H, 12.0.

x-p-Tolylbehenic acid. Saponification of 25 g. of the foregoing ester with potassium hydroxide as above afforded 18 g. of a viscous oil, which deposited a crystalline mass on prolonged standing in the refrigerator. This gave on recrystallization from light petroleum, 2.5 g. of waxy colorless leaflets, m.p. 57°. Oxidation with potassium permanganate in alkaline solution yielded terephthalic acid.

Anal. Calc'd for $C_{29}H_{50}O_2$: C, 80.9; H, 11.6. Found: C, 80.6; H, 11.6.

Addition of ethylbenzene to ethyl erucate. The reaction was performed as usual, with 92 g. of ethyl erucate, 55 g. of ethylbenzene, and 55 g. of aluminum chloride. Yield, 33 g. (27%) of *ethyl ethylphenylbehenate,* a pale yellow oil, b.p. 241–243°/0.4 mm., n_D^{25} 1.4802.

Anal. Calc'd for $C_{32}H_{56}O_2$: C, 81.4; H, 11.9. Found: C, 81.2; H, 11.9.

Alkaline saponification afforded *ethylphenylbehenic acid* as an oil, n_D^{31} 1.4931, which partly solidified in the refrigerator.

Anal. Calc'd for $C_{30}H_{52}O_2$: C, 81.1; H, 11.7. Found: C, 81.0; H, 11.9.

Addition of diphenyl to ethyl erucate. This reaction was effected with 92 g. of ethyl erucate and 60 g. of diphenyl (in carbon disulfide solution) in the presence of 55 g. of aluminum chloride. Yield, 35 g. (25%) of *ethyl xenylbehenate,* a pale yellow viscous oil, b.p. 263–264°/0.3 mm., n_D^{25} 1.5363.

Anal. Calc'd for $C_{36}H_{56}O_2$: C, 83.1; H, 10.8. Found: C, 83.0; H, 11.0.

The *xenylbehenic acid* obtained therefrom was a viscous oil, n_D^{25} 1.5361, from which no solid product with sharp m.p. could be isolated.

Methyl anisylbehenate. To a mixture of 60 g. of methyl erucate and 60 g. of anisole, 36 g. of aluminum chloride was added in small portions; the dark brown mixture was kept for two hours at room temperature, then warmed at 45–50° for a further hour. Yield, 27 g. (34%) of a pale yellow oil, b.p. 265–268°/0.5 mm., n_D^{31} 1.4889.

Anal. Calc'd for $C_{30}H_{52}O_3$: C, 78.3; H, 11.3. Found: C, 78.2; H, 11.3.

The *acid* obtained on saponification of this ester was an oil; demethylation by refluxing with pyridine hydrochloride yielded a *hydroxyphenylbehenic acid* which was a semi-solid mass.

Methyl veratrylbehenate. A similar reaction, performed with 60 g. of methyl erucate, 66 g. of veratrole, and 35 g. of aluminum chloride, yielded 25 g. of *methyl veratrylbehenate,* a viscous oil, b.p. 281–283°/0.5 mm., n_D^{31} 1.4764.

Anal. Calc'd for $C_{31}H_{54}O_4$: C, 75.9; H, 11.0. Found: C, 75.8; H, 11.3.

The corresponding *acid* was a viscous oil from which no solid product with sharp m.p. could be isolated; its demethylation by means of pyridine hydrochloride afforded a waxy product with pronounced antioxidant properties.

2-Behenonaphthone (IV). To a water-cooled solution of 40 g. of behenoyl chloride (prepared in quantitative yield from behenic acid and thionyl chloride) and 13 g. of naphthalene in 100 ml. of nitrobenzene, 15 g. of powdered aluminum chloride was added portionwise with stirring, and the mixture was left overnight. Dilute hydrochloric acid then was added, the nitrobenzene was removed by steam distillation, and the residue was taken up in benzene. The benzene solution was washed with water, dried over sodium sulfate, the solvent distilled off, and the residue fractionated in a high vacuum. The portion boiling at 300–365°/1 mm., crystallized from ethanol in fine, colorless needles, m.p. 75°. Yield, 8 g. The constitution of this ketone was deduced from former experiments with other acid chlorides.[6]

Anal. Calc'd for $C_{32}H_{50}O$: C, 85.3; H, 11.1. Found: C, 85.0; H, 11.3.

2-Behenothienone (V). To a water-cooled solution of 40 g. of behenoyl chloride and 15 g. of thiophene in 100 ml. of carbon disulfide, 26 g. of stannic chloride was added portionwise with stirring, and the mixture was refluxed for one hour on the water-bath. Dilute hydrochloric acid then was added, and the reaction product was taken up in chloroform; the chloroform solution was washed with water and dried over sodium sulfate, and the residue was fractionated in a high vacuum (250–270°/1 mm.). The ketone recrystallized from light petroleum in shiny, colorless leaflets, m.p. 67°; yield, 11 g.

Anal. Calc'd for $C_{26}H_{46}OS$: C, 76.8; H, 11.3. Found: C, 76.5; H, 11.2.

2-Erucothienone (VI). This ketone was similarly prepared from 10 g. of thiophene, 25 g. of erucic acid chloride (prepared from the acid with thionyl chloride), and 20 g. of

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[4] Buu-Hoï and Séailles, Jr., *J. Org. Chem.*, **20**, 606 (1955).

[5] Marcusson, *Angew. Chem.*, **33**, 234 (1920).

[6] Buu-Hoï and Cagniant, *Bull. soc. chim.*, [5] **11**, 307 (1945).

stannic chloride in 100 ml. of carbon disulfide. Yield, 7 g. of a product, b.p. 265–275°/1 mm., crystallizing from ethanol in waxy, colorless needles, m.p. 50°.

Anal. Calc'd for $C_{26}H_{44}OS$: S, 7.9. Found: S, 8.2.

1-Methoxy-2-behenonaphthone (VII). A solution of 2.5 g. of 1-hydroxy-2-behenonaphthone[4] and 1 g. of potassium hydroxide in ethanol was refluxed with 1.2 g. of methyl iodide for 2 hours. After cooling, water was added, and the precipitate was recrystallized from ethanol, giving lustrous, colorless leaflets, m.p. 83°; yield, 2.5 g.

Anal. Calc'd for $C_{33}H_{52}O_2$: C, 82.5; H, 10.8. Found: C, 82.3; H, 11.0.

2-Methoxy-5-methylbehenophenone was similarly prepared from 2 g. of the corresponding hydroxy ketone; this compound crystallized from ethanol in silky, colorless needles, m.p. 76°.

Anal. Calc'd for $C_{30}H_{52}O_2$: C, 81.1; H, 11.7. Found: C, 80.8, H, 11.7.

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