[CONTRIBUTION FROM THE CHEMICAL LABORATORY, UNIVERSITY OF TORONTO]

Determination of Geometric Isomer Composition by Methoxymercuration. Oleic and Elaidic Esters

BY THELMA CONNOR AND GEORGE F. WRIGHT

The *cis* isomer, in addition reactions involving the double bond, usually reacts faster than the *trans* form. This is characteristic of bromine,[1] hydrogen and bisulfite addition, as well as of oxidation and methoxymercuration.[2] It occurred to us that methoxymercuration might serve as an analytical tool for determination of *cis:trans* ratios in mixtures of compounds such as ethyl oleate and ethyl elaidinate. The boiling points, densities, refractive indices and viscosities of this pair are very close together, and melting points of the mixtures are too indefinite to be of reliable value.

Methanol is the preferred solvent for this addition because mercuric acetate solvolysis is less than in the higher alcohols. We soon found, however, that ethyl oleate reacted much too rapidly in methanol for convenient rate study at the concentration required for the thiocyanate titration.[2] Of the several known inhibitors,[3] acetonitrile was ineffective and pyridine caused such disagreeable emulsions and fading endpoints as to be impractical. Since the small temperature coefficient discouraged investigation of rates at lower temperatures we decided to reduce the reagent concentrations to $^1/_{50}$ of the 0.2 *M* solutions used previously and to determine the unconsumed mercury by dithizone titration.[4]

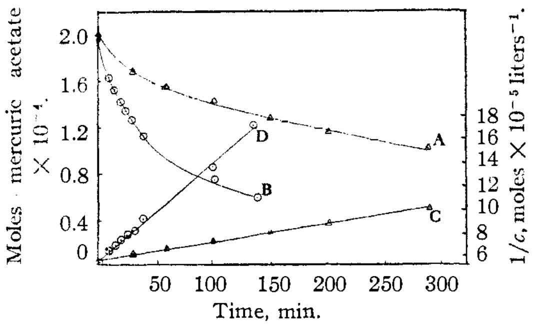

Fig. 1.—Kinetics, oleic (B, C) and elaidic (A, D) ester methoxymercuration.

Reference to Fig. 1 shows that curves A and B represent mercuric acetate consumption in the elaidinate and oleate reactions, respectively, while C and D are the corresponding reciprocal concentrations with respect to time. The rate constants may be calculated up to half life as $3.4 \pm 0.3 \times 10^{-4}$ for ethyl oleate and $0.8 \pm 0.2 \times 10^{\pm 4}$ for ethyl elaidinate, but the *trans* ester rate constant drops off badly thereafter. Reasonable constancy does, however, prevail up to one-third life and this time was used in the subsequent analytical work with mixtures.

Table I shows the one-third life periods for a series of ethyl oleate–ethyl elaidinate mixtures.

TABLE I

PER CENT. ETHYL ELAIDINATE VERSUS ONE-THIRD REACTION LIFE 2×10^{-4} MOLE ESTER PLUS 2×10^{-4} MOLE MERCURIC ACETATE IN 50 ML. VOLUME WITH METHANOL AT 24.75°

Actual % ethyl elaidinate	$T_{1/3}$, min.	Log $T_{1/3}$	Estimated % ethyl elaidinate
0	24.0	1.380	0
28	37.8	1.578	27.0
30	39.5	1.597	30.5
50	53.0	1.724	47.0
60	61.0	1.785	56.0
66	78.2	1.893	69.5
80	93.6	1.971	80.5
100	128.0	2.107	100.0

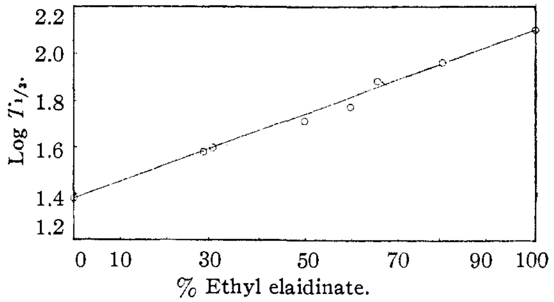

Fig. 2.—Log $^1/_3$ life periods *vs. cis-trans* composition oleic–elaidic ester mixtures.

The logarithms of these times values are plotted against the composition in Fig. 2 and a straight line drawn among these points. The maximum error in composition as estimated from this graph is about 4%. While this can be and was improved by increased skill in analysis it must be pointed out that very large errors can be introduced if catalysts, notably peroxides, are not eliminated from the esters prior to methoxymercuration. Furthermore Dr. A. R. Gordon of this Laboratory has pointed out to us that the linear log $T_{1/3}$ plot against *cis-trans* composition is conveniently a fortuitous approximation to the almost-flat curve calculable from these parameters, of a mixture of geometric isomers which are competing for an equimolar quantity of mercuric acetate.[5] The

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(1) C. Freudenberg, "Stereochemie," Franz Deuticke, Leipzig, 1933, p. 508.

(2) G. F. Wright, THIS JOURNAL, **57**, 1993 (1935).

(3) A. M. Birks and G. F. Wright, *ibid.*, **62**, 2412 (1940).

(4) C. O. Stonestreet and G. F. Wright, *Can. J. Research*, **18**, 246 (1940).

(5) It may be observed that deviation from linearity in Fig. 2 is greatest around 50% composition where the ratio of *cis* to *trans* consumption will be largest.

error is, however, minimized at the start when the amount of available mercuric acetate is large. The choice of one-third life during these experiments was adequate for the concentrations which we used. However the dithizone titration is applicable to reaction at higher dilution, where the slower rate makes shorter fractional reaction lives easier to determine. Improvement in precision during analysis for geometric isomer content by this method will therefore probably result by choice of reaction life less than one-third.

The products isolated from methoxymercuration of ethyl oleate and elaidinate were non-crystallizable oils. These might have been expected in view of the observations of Stirton and Peterson,[6] who believed they obtained structural isomers on addition of phenol to oleic acid. While the addition of methoxymercuric acetate has heretofore always been found to be specific with respect to the positions occupied by the entering groups, it is not surprising that the exception should be found with these fatty esters containing a double bond in the center of a long hydrocarbon chain.

Proof that the methoxymercurial from oleic acid was indeed a mixture was established by iodination, followed by treatment with alcoholic potassium hydroxide. The ketostearic acid (identified by its semicarbazone which could be reduced to stearic acid) was evidently a mixture since its melting point was unsharp at 71–72° and this is well below the 82 and 83° reported by Robinson[7] for 10-keto-and 9-keto-stearic acids. In this connection it should be noted that the keto-stearic acid (m. p. 75–76°) by action of mercuric acetate on stearolic acid[8] probably also is a mixture.

Experimental

Reagents.—The oleic acid was purified by the method of Skellon[9] and then fractionally crystallized to a setting point of 13°. Elaidic acid was crystallized from ethanol at −7° until it melted at 44.5°. Both were esterified in ether with diazoethane. The esters were washed with aqueous Mohr salt, dried under nitrogen with magnesium sulfate and distilled under 10^{-3} mm. pressure. The refractive indices of the ethyl oleate and elaidinate were $n^{25}\text{D}$ 1.4474 and $n^{25}\text{D}$ 1.4480, respectively.

The methanol was purified under nitrogen by the method of Bjerrum and Lund[10] and a single 5-liter preparation was used throughout this work. Likewise the same lot of Mallinckrodt mercuric acid was used exclusively.

Estimation of Relative Rates.—Mercury complexes of the fatty acids have been reported previously.[11] Our preliminary studies with the free acids showed that oleic acid reacted about four times faster than elaidic acid with mercuric acetate in ethanol. Oleic acid also reacted about four times faster in methanol than in ethanol at 24°. The temperature coefficient was found to be comparatively low, since the reaction in ethanol was approximately doubled from 24 to 82°.[12]

Analytical Procedure.—All glassware was rinsed with dilute Mohr salt solution, distilled water and pure methanol. Reactions were carried out in 50-ml. volumetric flasks equipped above the calibration mark with a closed side arm into which was placed the weighed ester in methanol solution. The methanolic mercuric acetate solution which was placed in the body of the flask was prepared from 0.2 g. mercuric acetate shaken with 10 ml. methanol and then centrifuged. The clear solution was pipetted into a 50-ml. volumetric flask, made up to volume with methanol and then standardized by withdrawal of a 1-ml. aliquot into 500 ml. of water. Then 10 ml. of this solution was analyzed with dithizone.[4]

Two $\times 10^{-4}$ mole of this methanolic mercuric acetate was added to the reaction flask and made up to 50 ml. at 24.75°. The ester was then washed in from the side-arm and a 1-ml. aliquot withdrawn into a separatory funnel containing 10 cc. of water. The pipet was rinsed with 2 cc. of chloroform and 2 cc. of water into the separatory funnel. The aqueous layer was extracted with this and four more 2-cc. portions of chloroform, and then made up to 100 ml. with water. A 10-ml. aliquot was then titrated, simultaneously with a standard mercuric acetate solution, and both in separatory funnels, with a saturated dithizone solution in carbon tetrachloride to the *first* green tint in the carbon tetrachloride layer. Non-extractable impurities from the sample tend toward emulsion formation in the carbon tetrachloride layer, and this complicates the necessary separation of the spent dithizone layer before fresh addition can be made from the buret.

Keto-stearic Acid.—Into a solution of 12.4 g. (0.04 mole) of ethyl oleate in 100 cc. of methanol was dissolved 12.8 g. (0.04 mole) of mercuric acetate. After twelve hours the whole was filtered into 200 cc. of 10% aqueous sodium chloride. After several hours the oil was taken up in 60 ml. chloroform. This solution was dried with Drierite and then treated with 11.5 g. (0.045 mole) of iodine in 100 cc. of chloroform. After fifteen hours the volume of the suspension was reduced to 60–70 cc. under vacuum, and the red mercuric salt was filtered off. The filtrate was washed twice with 50-cc. portions of 2% sodium sulfite and then dried with Drierite. Evaporation of the solution left 15 g. of a yellow oil. This was boiled for twelve hours under reflux with 50 cc. of 20% alcoholic potassium hydroxide. The alcohol was removed under vacuum, the residue dissolved in water and acidified with hydrochloric acid. The curd was separated, dissolved in chloroform and washed twice with 0.5% hydrochloric acid. Vacuum evaporation of the chloroform solution left 10.6 g. of a yellow solid melting from 40 to 62°. Crystallization from petroleum ether (b. p. 40–60°), methanol and twice from cyclohexane left 2.9 g. melting at 71–72°. This was increased to 73–74° by two crystallizations from nitromethane.

Anal. Calcd. for $C_{18}H_{34}O_3$: C, 72.4; H, 11.5; neut. equiv., 298. Found: C, 72.1; H, 11.7; neut. equiv., 296.

The semicarbazone was prepared in ethanol in 72% yield, m. p. 99–104°. Repeated crystallizations from chloroform raised this melting point to 105–106°.

Anal. Calcd. for $C_{19}H_{37}N_3O_3$: C, 64.2; H, 10.4; N, 11.8. Found: C, 64.2; H, 10.1; N, 11.8.

This semicarbazone was converted to crude stearic acid, m. p. 64–66°, in 80% yield by heating to 200° for eight hours, 0.25 g. (8×10^{-4} mole) in 5 cc. of a sodium ethoxide solution prepared from 0.25 g. (0.11 atom) of sodium. Two crystallizations from ethanol raised this melting point to 70–71° and a mixed melting point with authentic stearic acid was not lowered.

Summary

1. The methoxymercuration analysis for *cis-trans* ratios in geometric isomer mixtures is ac-

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[6] A. J. Stirton and R. F. Peterson, *Ind. Eng. Chem.*, **31**, 856 (1939).

[7] G. M. Robinson and R. Robinson, *J. Chem. Soc.*, **128**, 2204–2209 (1926).

[8] W. W. Middleton, R. G. Berchem and A. Barrett, THIS JOURNAL, **49**, 2264 (1927).

[9] J. H. Skellon, *J. Soc. Chem. Ind.*, **50**, 131–134 (1931).

[10] J. Bjerrum and H. Lund, *Ber.*, **64**, 210 (1931).

[11] (a) W. Schoeller, W. Schrauth and R. Struensee, *Ber.*, **43**, 695 (1910); (b) S. H. Bertram, *Rec. trav. chim.*, **46**, 397 (1927).

[12] Unpublished with Lois Retallack, McGill University, 1936.

curate within 4%, since the relationship of one-third reaction life to compositions is linear within this error.

2. A greater accuracy may be attained by use of shorter reaction life periods, and this is possible with the higher dilution of mercury which can be titrated with the dithizone reagent.

3. A mixture of methoxy chloromercurials is evidently produced owing to the weak directive influence of the centralized double bond in oleates and elaidinates.

TORONTO, CANADA RECEIVED JULY 13, 1945

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

The Catalytic Dehydrogenation of 1-Substituted 1,2,3,4-Tetrahydronaphthalene Derivatives

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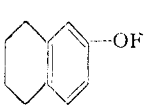
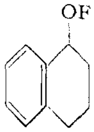
The work herein reported is a continuation of studies designed to obtain more information about the fate of oxygenated functions in hydroaromatic compounds when submitted to liquid phase catalytic dehydrogenation. In a previous report[2] the dehydrogenation over palladium-on-charcoal of a series of 2-substituted-5,6,7,8-tetrahydronaphthalenes, A, was described. In this paper similar studies on 1-substituted 1,2,3,4-tetrahydronaphthalenes, B, are discussed. Thus not only is the position of the oxygenated functions (OF) on the nucleus changed but also the relative positions of the hydrogen to be removed and the oxygenated functions are different.



A



B

Throughout the discussions Ar will be used to designate the 5,6,7,8-tetrahydro-2-naphthyl radical, R, the 1,2,3,4-tetrahydro-1-naphthyl radical, and R', the 1-naphthyl radical.

The results obtained with two methyl esters, $RCOOCH_3$, I, and RCH_2COOCH_3, II, three ketones, $RCOCH_3$, III, RCH_2COCH_3, IV, and $RCH_2CH_2COCH_3$, V, and two alcohols and their acetates, RCH_2OH, VI, RCH_2CH_2OH, VII, RCH_2OCOCH_3, VIII, and $RCH_2CH_2OCOCH_3$, IX, are summarized in Table I.

TABLE I

No.	Compound R =	Flask	Temp., °C.	Time, hr.	% H_2[a]	Products R =	% Yield[b]
I	$RCOOCH_3$	A	306–315	8.0	82.8	$R'COOH$	74.7
II	RCH_2COOCH_3	A	260–310	5.2	99.4	$R'CH_2COOH$	90.9
III	$RCOCH_3$	B	288–310	7.0	19.0	$R'COCH_3$	14.7[c]
						$RCOCH_3$	70.0[c]
IV	RCH_2COCH_3	B	290–315	10.0	85.8	$R'CH_2COCH_3$	84.2
V	$RCH_2CH_2COCH_3$	B	325–327	7.5	47.3	$R'CH_2CH_2COCH_3$	16.0[d]
						$RCH_2CH_2COCH_3$	57.0[d]
						$R'CH_3$	14.0
VI	RCH_2OH	B	275–300	13.0	53.6[2]	$R'CH_3$	4.0
						$R'H$	95.6
VII	RCH_2CH_2OH	B	280–303	8.6	75.9[e]	$R'CH_3$	76.7
						$R'CH_2CH_2OH$	12.0
VIII	RCH_2OCOCH_3	B	290–295	5.0	25.8	$R'CH_2OH$	26.0
						$R'CH_3$	10.0
						RCH_3	14.0
IX	$RCH_2CH_2OCOCH_3$	B	290–302	5.7	76.0	$R'CH_2CH_2OH$	62.5
						$R'CH_2CH_3$	28.3

[a] The theoretical amount of hydrogen in each case is calculated as two moles per mole of hydroaromatic compound. [b] The yields represent purified material except as noted. [c] Yields estimated from index of refraction measurements. [d] Yields estimated from distillation data. [e] The theoretical amount of gas is four moles ($3H_2 + 1CO$) per mole.

Experimental[3]

Methyl 1,2,3,4-Tetrahydro-1-naphthoate, I.—In a typical experiment 101 g. of ethyl 3,4-dihydro-1-naphthoate,[4] 70 cc. of ethyl alcohol and 15 g. of powdered nickel-on-kieselguhr catalyst were charged into a bomb under 1000 lb. pressure of hydrogen. At 140° reduction was complete after two hours to yield 96.5 g. (94.6%) of ethyl 1,2,3,4-tetrahydro-1-naphthoate, b. p. 115° (0.5–1.0 mm.). On hydrolysis, the free acid, m. p. 80–81°, was obtained.[5] This acid was also obtained in 94% yield by reduction of

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[1] This work was taken from the thesis submitted by Fr. T. J. O'Leary to The Ohio State University in partial fulfillment of the requirements for the Ph.D. degree, June, 1945.

[2] Newman and Zahm, THIS JOURNAL, **65**, 1097 (1943).

[3] All melting points corrected. Microanalyses marked [a] by J. A. Curtiss, [b] by S. R. Olsen, [c] and by the Arlington Laboratories, Fairfax, Virginia.

[4] Fieser and Holmes, THIS JOURNAL, **58**, 2319 (1936).

[5] Baeyer and Schroder, *Ann.*, **266**, 184 (1891).