reagents were made into 2% aqueous solutions containing 2% sulphuric acid and held in covered beakers for 3 hours at 150°C. and 180°C. in gas-heated laboratory autoclaves charged with a little water. The aqueous suspensions of the reagents so treated were used for splitting tallow at 100°C. and 150°C., applying in each case 1% reagent, 1% sulphuric acid, and 100% water calculated on the fat basis.

Parallel tests were run with reagents not subjected to previous heating. Some typical results are shown in Table II and indicate that the preheating of the old type of Twitchell reagent to 150°C. (approximately 55 lb. per square inch pressure) impaired to some extent its performance in the subsequent hydrolysis of tallow at 100°C. whereas the "Kontakt" reagent remained unaffected. Preheating to 180°C. reduced the efficiency of both reagent types quite distinctly. At 150°C. however hydrolysis was practically completed in 3 hours, both with previously heated and unheated reagents, a circumstance which denotes a remarkably short reaction time considering that no stirring was applied. The use of 0.5% ZnO as a catalyst gave under similar conditions a 34% split as compared with 90% achieved with Twitchell catalysts. When the sweet water from the Twitchell hydrolysis was removed and 50% of fresh water and 0.5% sulphuric acid but no more reagent was added to the fat, a further hour of heating at 150°C. yielded a 96% split. These results were obtained independent of the type of Twitchell reagent employed. The chief obstacle against replacing basic catalysts in the autoclave process with Twitchell reagents appears therefore to be the corrosive action of diluted sulphuric acid on metals used in the construction of autoclaves. Despite statements to the contrary a small amount of this acid seems to be essential for satisfactory working of the Twitchell reagents, and even if free sulphonic acids only were used, their corrosive action on metals would also lead to difficulties. Nevertheless the advantages of a Twitchell process carried out under moderate pressures seem so evident that one can only wish for an early solution of the problem of finding a sufficiently resistant material. This would at the same time facilitate the developing of a continuous Twitchell process.

TABLE II

Effect of Temperature on Twitchell Catalysts (Kontakt Reagent Denoted "A" and Twitchell Reagent "B")

Materials: Tallow with 5.5% F.F.A.; 1% catalyst; 1% H_2SO_4; 100% H_2O

Time	Splitting Degree, %									
	Hydrolysis at 100°C. with catalysts						Hydrolysis at 150°C. with catalysts			
	Preheated to 180°C. 3 hours		Preheated to 150°C. 3 hours		Untreated		Preheated to 150°C. 3 hours		Untreated	
	"A"	"B"	"A"	"B"	"A"	"B"	"A"	"B"	"A"	"B"
hours										
3	22	6	40	6	41	6	92	91	92	90
6	46	9	62	10	61	10				
12	53	42	71	50	71	58				
18	75	61	85	70	85	82				
24	75	65	88	77	88	82				

Summary

Velocity constants of the Twitchell hydrolysis have been calculated from recently published experimental data and found to increase approximately twofold for a 10°C. rise around the temperature of 100°C. This seems to indicate that the rate of reaction is governed by hydrolysis rather than by diffusion of water into the fat phase (and of glycerol into water).

Preheating to 150°C. reduces the efficiency of the old type of Twitchell catalyst but does not affect the "Kontakt" reagent. The increasing of the temperatures from 100°C. to 150°C. substantially accelerates the hydrolysis independent of the type of Twitchell reagent employed.

Acknowledgment

The author is indebted to Miss H. E. Watt for technical assistance.

REFERENCES

1. Cox, C. B., Trans. Inst. Chem. Engrs. (London), *27*, 123-137 (1949).
2. Hartman, L., New Zealand J. Sci. Technol. B, *33*, 5-10 (1951); Nature, *167*, 199 (1951).
3. Lascaray, L., J. Am. Oil Chem. Soc., *29*, 362-366 (1952).
4. Lascaray, L., Anales Fis. y Quim., *41*, 878-900 (1945); Ind. Eng. Chem., *41, 786-790 (1949) and others.*
5. Suen, T.-J., and Chien, T.-P., Ind. Eng. Chem., *33*, 1043-1045 (1941).
6. Vereinigte Chem. Werke A.-G., Ger. Pat. 481,088 (1925).

[Received December 29, 1952]

The Chemical Utilization of Fats and Oils. II. A New Reaction of Glycerides

R. M. SILVERSTEIN, R. D. ENGLERT, and L. M. RICHARDS, Stanford Research Institute, Stanford, California

THE usual method of preparing aralkyl ketones consists of the condensation of acids, acid chlorides, or acid anhydrides with aromatics in the presence of a catalyst such as aluminum chloride. This paper describes the direct condensation of glycerides with benzene to give aralkyl ketones in yields comparable with those obtained by conventional means.

Experimental

The aluminum chloride-catalyzed condensation was accomplished as follows (Table I): The glyceride was dissolved in a large excess of benzene. About one-third of the aluminum chloride to be used was added portion-wise during the first half-hour on the steam bath, and the balance of the catalyst was introduced thereafter. The mixture was shaken vigorously at frequent intervals during the reaction period. After standing overnight, it was drowned in ice water acidified with hydrochloric acid. The organic layer was separated, and the aqueous layer was extracted with ether. The combined organic portions were washed with water and dried. The ketones were isolated by distillation.

TABLE I

Condensation of Glycerides Using Aluminum Chloride

Exp. No.	Reactants	Conditions	Conversion[a]	Yield	Remarks
			%	%	
1	21.7 g. (0.1 equiv.) hydrog. coconut oil 78 g. (1 mole) benzene 40 g. (0.3 mole) $AlCl_3$	2 days at room temp. 2 hrs. on steam bath	30	ND[b]	m.p. = 28-32°C.[c]
2	43.4 g. (0.2 equiv.) hydrog. coconut oil 156 g. (2 moles) benzene 80 g. (0.6 mole) $AlCl_3$	1 hr. at room temp. 3 hrs. on steam bath	68	ND	115-170°C./1 mm.[d]
3	43.4 g. (0.2 equiv.) hydrog. coconut oil 156 g. (2 moles) benzene 27 g. (0.2 mole) $AlCl_3$	4 hrs. on steam bath	Negligible		
4	43.4 g. (0.2 equiv.) hydrog. coconut oil 156 g. (2 moles) benzene 56 g. (0.42 mole) $AlCl_3$	4 hrs. on steam bath	ND	ND	No acids were precipitated from an ether solution of product on introduction of dry NH_3
5	57.2 g. (0.2 equiv.) hydrog. acidless tallow 156 g. (2 moles) benzene 56 g. (0.42 mole) $AlCl_3$	Heat on steam bath for 2 hrs. then overnight at room temperature	39	65	Obtained 35% recovery of glycerine.
6	57.2 g. (0.2 equiv.) hydrog. acidless tallow 156 g. (2 moles) benzene 66.7 g. (0.5 mole) $AlCl_3$	Heat on steam bath for 4 hrs. then overnight at room temperature	45	64	45% glycerine recovery
7	660 g. (2.3 equiv.) hydrog. acidless tallow 1794 g. (23 moles) benzene 766 g. (5.75 moles) $AlCl_3$	Heat on steam bath for 6 hrs. then overnight at room temperature	63	86	90-255°C./2 mm. 29% glycerine recovery

[a] The percentage conversion is based on the quantity of condensation product obtained compared with theory, and the percentage yield is based on the quantity of product and the fraction of acids consumed.

[b] Not determined.

[c] Melting point on material recrystallized once from methanol. The 2,4-dinitrophenylhydrazone melted at 97-98°C., and a mixed melting point with laurophenone-2,4-dinitrophenylhydrazone (mp. 98-100°C.) was 97-99°C.

[d] A solid product crystallized from a methanol solution of the distillate. Analysis—Calc'd as laurophenone: C, 83.2; H, 10.8. Found: C, 83.0; H, 10.8.

Glycerine was recovered by making the aqueous solution slightly basic, filtering the precipitated aluminum hydroxide, and washing with water. The filtrate and washings were evaporated to dryness *in vacuo,* and the residual salts were leached with methanol. After filtration, the methanol was evaporated and the process repeated until the crude glycerine was fairly free of salts.

As an example, 660 g. (2.3 equiv.) hydrogenated acidless tallow, 1,800 g. (23 moles) benzene, and 766 g. (5.75 moles) aluminum chloride were allowed to react, and the mixture was worked up in accordance with the above method. A 530-g. fraction distilling at 90-255°C./2.0 mm. was collected, leaving a 162-g. residue. The glycerine recovered weighed 12.8 g. The distillate and residue were then analyzed. There remained about 0.22 equivalent of acyl component unaccounted for and 35 g. of residue as unknown material.

	Equivalents	Weight, grams
Distillate (530 g.)		
Acids (by acid-base titration)	0.19	52
Ketones (by difference)	1.44	478
Residue (162 g.)		
Acids (by acid-base titration)	0.005	1.3
Ketones (hydroxylamine method [9])	0.011	3.7
Glycerides (saponification and titration)	0.43	122

This experiment may be summarized as:

% conversion	63
% yield	86
% glycerine recovery	29

Glycerides were condensed with benzene in the presence of hydrogen fluoride in the same manner as has been described in previous work for the condensation of fatty acids (4) (Table II).

Discussion

Esters can react with aromatics by two possible paths, *i.e.*, acylation or alkylation. There are a number of examples in the literature of the alkylation reaction; however few references are made to the acylation.

Norris and Sturgis (7) have pointed out that either ketones or hydrocarbons (or both) are formed in the reaction of esters with aromatics depending upon the relative bond strengths in the ester, the type of ester, the temperature of reaction, and the amount of aluminum chloride. The acylation reagents were limited to esters of monohydric alcohols. Cryer (3) and Cox (2) have studied similar reactions.

A German patent (5) covered the production of nuclear alkylated aralkyl ketones by the action of esters on aromatic compounds of the benzene series in the presence of aluminum chloride. The use of two moles of aluminum chloride for each ester group was specified. The only example of an ester of a polyhydric alcohol cited was the reaction of benzene with glycol diacetate to give bis (p-acetylphenyl)-ethane.

Bowles (1) described the condensation of halogenated aromatic hydrocarbons with glycerides, using zinc chloride. He stated that a dehydrohalogenation occurs between the two reactants rather than an acylation of the aromatic by the glyceride. This reaction would not be expected since it has been shown that stearic acid and stearoyl chloride condense with chlorobenzene without dehydrohalogenation to give p-chlorostearophenone (6).

Robinson (8) has described the condensation of natural and synthetic esters of saturated monocarboxylic acids and monohydric alcohols with aromatics, especially phenols of the benzene and naphthalene series.

In the present work the aralkyl ketones were the major products.

The condensation of glycerides with benzene in the presence of aluminum chloride proceeded sluggishly at room temperatures but smoothly at temperatures in the range of 40-80°C. At least 2.1 moles of aluminum chloride for each equivalent of glyceride was necessary for the condensation to give a good yield of aralkyl ketone. At a ratio of 1:1 only a negligible

TABLE II

Condensation of Glycerides Using Hydrogen Fluoride

Exp. No.	Reactants	Conditions	Conversion	Remarks
			%	
1	26 g. (0.12 equiv.) coconut oil 86 g. (1.1 moles) benzene 330 g. (16.5 moles) HF	Overnight at room temperature and atmospheric pressure	0	
2	47.2 g. (0.22 equiv.) coconut oil 19.5 ml. (0.22 mole) benzene 414 g. (20.7 moles) HF	*Heat in bomb in steam bath for 3 hrs.*	7[a]	108-216°C./1 mm.
3	47.2 g. (0.22 equiv.) coconut oil 19.5 ml. (0.22 mole) benzene 298 g. (14.9 moles) HF	Heat in bomb at 125°C. for 3 hrs.	19	106-220°C./1 mm.
4	47.2 g. (0.22) equiv.) cocoonut oil 35.8 ml. (0.4 mole) benzene 318 g. (15.9 moles) HF	Heat in bomb at 100°C. for 5.5 hrs.	19	84-216°C./1 mm.

[a] The 2,4-dinitrophenylhydrazone of the mass was prepared and recrystallized several times from methanol. It melted at 99-100°C. and did not depress the melting point of a known sample of laurophenone-2,4-dinitrophenylhydrazone (mp. 99-100°C.). Analysis—Calc'd: N, 12.72. Found: N, 12.40, 12.43.

amount of product was isolable. Ratios of 2.1:1 to 3:1 were effective.

The condensation employing hydrogen fluoride produced only traces of ketones at room temperatures and atmospheric pressure, and only poor yields at temperatures in the range of 70-125°C. and autogenous pressures.

Alkylation with glycerol as a probable side-reaction may account for the low glycerol recoveries and for the residue of unknown materials.

Summary

The direct condensation of glycerides with benzene in the presence of aluminum chloride or hydrogen fluoride to produce aralkyl ketones has been described.

Acknowledgment

This work was supported by the Purex Corporation Ltd., Southgate, Calif.

REFERENCES

1. Bowles, A. F., U. S. Patent 2,144,324 (1939).
2. Cox, E. H., J. Am. Chem. Soc., *52,* 352-358 (1930).
3. Cryer, J., Trans. Roy. Soc. Canada, III (3), *19,* 29 (1925).
4. Englert, R. D., Silverstein, R. M., and Richards, L. M., Paper No. I (in press).
5. I. G. Farbenind, Ger. patent 637,384 (1936).
6. Martin, H., and Hirt, R., U. S. Patent 2,205,728 (1946).
7. Norris, J. F., and Sturgis, B. M., J. Am. Chem. Soc., *61,* 1413-1417 (1939).
8. Robinson, J. D., U. S. Patent 2,061,593 (1936).
9. Siggia, S., "Quantitative Organic Analysis Via Functional Groups," p. 17, New York, John Wiley and Sons Inc. (1949).

[Received March 18, 1953]

Report of the Spectroscopy Committee—1952-1953

THE Spectroscopy Committee in its November 15, 1948, report recommended a detailed spectrophotometric method for the analysis of fats and oils to the Society for its adoption. As a result, A.O.C.S. Tentative Method Cd 7-48 was issued as a part of A.O.C.S. methods. Following the work done in 1950 and 1951 additional recommendations concerning the method were made in the 1951 report of the Committee. As a result, the method was revised in May, 1951.

Present Work

The committee has done additional work during the past year and a half, following the procedure as revised in May, 1951. The object of this work was to check the precision of the method and to investigate additional details which seemed pertinent on the basis of previous work carried out. Accordingly, six samples were submitted to the committee members and were analyzed. The six samples submitted were:

Oil No.	Kind of oil	Iodine value	% Saturated acids*
1	Unhardened soybean oil	135.0	13.92
2	Hydrogenated soybean oil	106.4	14.87
3	Hydrogenated soybean oil	77.7	16.48
4	Fish oil	177.5	22.85
5	Fish oil+soybean oil (50% No. 1+50% No. 4)	155.3	17.80
6	Linseed oil	188.1	8.45

* Determined by the Southern Regional Research Laboratory, following a modification of the Bertram Oxidation method described by K. A. Pelikan and J. D. Von Mikusch in Oil and Soap *15,* 149-150 (1938).

These oils were analyzed at least in duplicate by all six members of the committee. The oils were analyzed first, following exactly the procedure outlined in the A.O.C.S Tentative Method Cd 7-48 as revised in May, 1951. They were then re-analyzed using a 45-min. isomerization time at 180°C. The composition of the samples was calculated in the former case, using the calculations set down in the A.O.C.S. method. The compositions were also calculated for the 45-min. isomerization, using data submitted by the Eastern Regional Research Laboratory and reported in a paper by Brice, Swain, Herb, Nichols, and Riemenschneider in the Journal of the American Oil Chemists' Society, July, 1952, Volume XXIX, pages 279-287. The data were recalculated for both the 25- and 45-min. isomerizations, making no background corrections when k'_{268} and k'_{315} were greater than one. The composition of samples 2 and 3 was also recalculated, using the debromination constants originally a part of the method as issued in 1948. All of these data are given in the attached five tables.

Conclusions

As a result of the work herein reported, several conclusions can be drawn:

a) Reasonably reproducible results, using A.O.C.S. Tentative Method Cd 7-48, revised May, 1951, can be obtained in the hands of experienced operators.

b) No particular increase in either precision or accuracy is obtained by using a 45-min. isomerization time.