benzoylethenol) was dissolved in 20 cc. of thionyl chloride, immediate reaction taking place. The mixture was refluxed for thirty minutes, and the solution then cooled and diluted with ligroin. The product crystallized and was recrystallized from chloroform–ligroin mixtures, m. p. 133–133.5° (corr.); yield 90% (the yield in the case of dibenzoylethenol was 50%).

Anal. Calcd. for $C_{16}H_{11}O_2Cl$; Cl, 13.1. Found: Cl, 13.1%.

Attempted hydrolysis by refluxing a water–dioxane solution, and reduction with zinc and glacial acetic acid at 50°, gave resinous products. When treated with methanol or ethanol (refluxing for a short time) almost quantitative yields of the corresponding diphenyl-4-alkoxy-3-butene-1,2-dione were obtained.

Summary

Phosphorus pentachloride reacts with various 2,5-diphenylfurans and saturated and unsaturated 1,4-diketones to give 2,5-diphenylchloro and dichlorofurans. Phosphorus pentabromide reacts analogously but with bromination of the alpha phenyl groups in the para positions. Under drastic conditions phosphorus pentachloride converts diphenyldichlorofuran into *cis*-dibenzoyldichloroethylene.

The mechanism of the reactions with unsaturated 1,4-diketones is discussed.

Thionyl chloride proved to be without the same degree of chlorinating and dehydrating action as phosphorus pentachloride but reacts similarly in some cases. It apparently adds to unsaturated 1,4-diketones, and reacts with dibenzoylmethoxy and hydroxy ethylenes to give 1,4-diphenyl-4-chloro-3-butene-1,2-dione.

University, Va. Received July 16, 1934

[Contribution from the Laboratory of Physiological Chemistry, The Ohio State University]

The Occurrence of Highly Unsaturated Fatty Acids in the Oils of Some Common Fowls and in Animal Fats

By J. B. Brown and C. C. Sheldon

For many years the belief has been general that the body fats and oils of land animals are composed principally of glycerides of oleic, stearic and palmitic acids. Furthermore, careful investigations have usually revealed the presence of small amounts of saturated acids of lower molecular weight than palmitic, as well as small amounts of linolic acid, $C_{18}H_{32}O_2$. Linolenic acid, $C_{18}H_{30}O_2$, has been found rarely in such fats; when it does occur, its origin has been in the diet.

The present investigation was stimulated by Eckstein's[1] discovery of arachidonic acid, $C_{20}H_{32}O_2$, in human body fat, the observation of Ellis and Isbell[2] and of Brown and Deck[3] that this acid occurs in lard, and the proof by Brown and Sutton[4] of the presence of acids of this type in butterfat. By reason of these results it was thought possible that highly unsaturated fatty acids, *i. e.*, acids with four or more double bonds, might occur rather generally in animal fats and oils.

Experimental demonstration of the presence of small amounts of highly unsaturated acids is comparatively simple, since either the acids or their methyl esters yield upon bromination in cold ether characteristic insoluble octa- or polybromides.

By the use of the above method twelve specimens of fowl oils and four of animal fats have been analyzed and the methyl esters of the fatty acids have been prepared and examined for highly unsaturated acids. Two specimens of goose oil gave ester bromides, definitely indicating the presence of linolenic acid; another specimen appeared to contain both linolenic acid and other acids more highly unsaturated, as did a sample of turkey oil. Two additional specimens of goose oil, four of chicken oil and two of duck oil yielded small amounts of ester bromides, the melting point and bromine content of which were close to the theoretical for the corresponding derivative of arachidonic acid. The ester bromides from specimens of lamb, veal and reindeer tallows gave melting points which are indicative of the presence of acids other than arachidonic, either more highly unsaturated or of higher molecular weight. Beef tallow yielded only a trace of bromides. From these results it seems probable that small amounts of highly unsaturated acids occur generally in animal fats and oils.

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(1) H. C. Eckstein, *J. Biol. Chem.*, **64**, 797 (1925).

(2) N. R. Ellis and H. S. Isbell, *ibid.*, **69**, 219, 239 (1926).

(3) J. B. Brown and E M. Deck, This Journal, **52**, 1135 (1930).

(4) J. B. Brown and T. S. Sutton, *J. Dairy Sci.*, **14**, 125 (1931).

Experimental Part

The several specimens of fats and oils were obtained from authentic sources. They were dried thoroughly by warming under reduced pressure. After analysis, a portion of each was converted into methyl esters by the usual process of methanolysis. They were analyzed by the usual methods. The polybromide numbers (percentage yield of polybromides) were determined by brominating weighed samples in cold ether. The precipitated bromides were thoroughly washed with cold ether, dried and weighed. Bromine was determined by the Parr peroxide bomb method. Calculations of the amount of arachidonic acid have been made by the method proposed by Brown[5] in those instances in which it was apparent from other data that arachidonic was the principal highly unsaturated acid present. This method takes into account the fact that pure methyl arachidonate gives a polybromide number of 77.6, which is only one-fourth that predicted by theory (301). Subsequent work in this Laboratory has shown this method of calculation to be essentially correct. The analytical results are shown in Table I.

Table I

Results of Examination of Fats and Oils and their Methyl Esters

		Fat		Methyl esters					
Specimen		Sapon. no.	Iodine no.	Sapon. no.	Iodine no.	Poly-bromide no.	Br in bromides, %	Arachi-donic, %	M. p. of bromides, °C.
1	Goose	194.3	84.5	192.4	82.1	3.26	61.99[a]	...	150–154
2	Goose	194.6	84.3	192.8	83.1	3.24	61.77	...	152–155
3	Goose	195.7	79.3	193.6	75.7	1.08	62.23	...	180–234
4	Goose	194.8	80.9	194.4	76.9	0.65	63.41	0.83	229–232 D[b]
5	Goose	195.3	78.4	194.8	74.6	.91	64.01	1.16	230–233 D
6	Chicken	195.6	76.8	195.2	73.8	.17	65.29	0.22	228–233 D
7	Chicken	195.8	76.9	195.0	73.9	.20	66.19	.26	234–235 D
8	Chicken	194.5	77.2	195.2	74.8	.19	66.03	.25	230–233 D
9	Chicken	195.5	76.7	194.2	74.3	.21	65.48	.27	231–234 D
10	Duck	196.2	74.5	196.1	69.8	.19	63.95	.25	225–229 D
11	Duck	196.0	79.1	194.6	74.4	.16	64.77	.21	232–233 D
12	Turkey	195.0	83.6	194.9	79.9	.49	63.07	...	165 (225–230)
13	Lamb	198.3	42.2	...	..	.16	66.53	...	245–250 D
14	Calf	200.9	42.6	...	..	.065	66.50	...	243–250 D
15	Beef	...	..	...	31.9	trace	...	...	Dec. at 250°
16	Reindeer	203.2	41.1	...	..	.15	66.45	...	238–240 D

[a] Theoretical bromine content: methyl hexabromostearate 61.98%; methyl octobromoarachidate 66.78%. [b] Decomposition.

Discussion of Results

The data in the preceding table require little discussion except to explain our deductions from the melting point behavior. Methyl hexabromostearate melts at 157–158°; the bromide of methyl arachidonate melts at 228–231° (uncorr.).[5] Information concerning other esters of this type is incomplete. In our studies in this Laboratory we have frequently obtained methyl ester bromides which melt between 235 and 250°. As a rule these contain higher percentages of bromine and have been considered to be derivatives of acids of higher unsaturation or of higher molecular weight. We have drawn similar conclusions here. Both melting point and bromine content of the bromides of the methyl esters of two of the specimens of goose fat definitely indicate the presence of linolenic acid. Whether or not this was of dietary origin could not be ascertained, since we had no record of the diet. The ester bromides of one additional specimen of goose oil and one of turkey oil sintered at 165–180°, etc., completely melting at 230°, giving reason to suspect the presence of traces of both linolenic acid and the more highly unsaturated acids. The other specimens of avian oils gave ester bromides melting between 228–235°, which is strongly indicative that the small amount of unsaturated acid present is mostly arachidonic. The ester bromides from the four specimens of animal fats melted definitely above 238°; the highly unsaturated acids from these fats probably belong to series more highly unsaturated or of higher molecular weight than arachidonic acid, possibly such acids as eicosapentenoic, $C_{20}H_{30}O_2$, docosatetrenoic, $C_{22}H_{36}O_2$, and docosapentenoic, $C_{22}H_{34}O_2$.

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(5) J. B. Brown, *J. Biol. Chem.*, **80**, 455 (1928).

As a result of this and of the work already cited we believe that small amounts of highly unsaturated fatty acids occur quite generally in animal fats.

Summary

1. Several animal fats and oils have been examined chemically for the presence of highly unsaturated fatty acids.
2. Linolenic acid was definitely indicated in two specimens of goose oil; it probably occurred along with highly unsaturated acids in another specimen of goose oil and in one of turkey oil.
3. Eight other specimens of avian oils were shown to contain 0.21 to 1.16% of highly unsaturated acid which was mostly arachidonic.
4. The four specimens of animal fats contained traces of highly unsaturated acids other than arachidonic.

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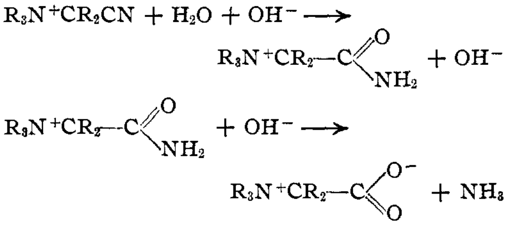
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Kinetics of the Alkaline Hydrolysis of the Betaine Amides

BY DANIEL B. LUTEN, JR., AND T. D. STEWART

In a recent paper Stewart and Korpi[1] reported the results of a study of the rates of hydrolysis to betaines of the corresponding betaine nitriles. The reaction proceeds according to the equations



$$R_3N^+CR_2CN + H_2O + OH^- \longrightarrow R_3N^+CR_2{-}C(=O)NH_2 + OH^- \quad (1)$$

$$R_3N^+CR_2{-}C(=O)NH_2 + OH^- \longrightarrow R_3N^+CR_2{-}C(=O)O^- + NH_3 \quad (2)$$

They assumed that in this case, as in the case of the ordinary aliphatic nitriles, the first of these steps is the slower so that it alone was being measured. They found that the rates were describable by differential equations involving fractional exponents, but which could not be derived from a reasonable mechanism for the reaction.

It has now been found for these betaine derivatives that, of the two steps in the hydrolysis, the first is actually much the faster. This paper presents the evidence for this statement and gives additional kinetic data which are relevant to the mechanism of Reaction (2) above. The description of most of the compounds used and the determination of their reactivities will be deferred to a later paper.

The First Step in the Hydrolysis, Nitrile to Amide.—The evidence proving that the reaction proceeds in two stages, of which the first is much the faster and has for its product the amide, may be summarized as follows

(1) In very dilute alkali the nitrile reacts with water to form a compound which gives the correct elementary analysis for the amide, has the same melting point as the amide prepared by an independent method, and whose melting point, when mixed with the independently prepared amide, suffers no depression.

(2) The product of the reaction of the nitrile in very dilute alkali is a solution which has the same refractive index as has a solution of the amide and alkali in the same concentrations, respectively.

(3) The independently prepared amide hydrolyzes to give ammonia at the same rate as the nitrile.

Experimental

(1) Preparation of Betaine Amides.—Iodoacetamide was prepared as described by von Braun[2] and with it trimethylamine and triethylamine were quaternized.

Anal. Calcd. for $C_5H_{13}ON_2I$: I, 52.01. Found: I, 51.80, 51.79. Calcd. for $C_8H_{19}ON_2I$: I, 44.37. Found: I, 43.98, 44.09.

For the trimethylbetaine amide iodide, the observed m. p. was 196°; the value in the literature[3] is 191°. For the triethyl derivative the observed m. p. was 155°, the value in the literature[3] is 150.5–152.5°.[4]

A substance having the same characteristics as the first

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[1] Stewart and Korpi, THIS JOURNAL, **54**, 3977 (1932).

[2] J. von Braun, *Ber.*, **41**, 2144 (1908).

[3] A. G. F. A. German Patent 292,545; *Chem. Zentr.*, II, 207 (1916).

[4] These derivatives and nearly all the others considered in this work decompose at or near the melting point. If the melting points are determined in the usual manner, the results obtained are dependent upon the time required for heating. Reasonably reproducible results were obtained only by making very rapid determinations, the sample being heated at the rate of fifteen degrees per minute until near the melting point and then at ten degrees per minute until fusion took place. As a check on all values, the melting point of $(C_2H_5)_2(CH_3)N^+CH_2CNI^-$ was always determined simultaneously. The values obtained are reproducible to within two or three degrees,