concentrated nitric acid according to the method of Berlande.[9] It melted sharply at 60°. We repeated the preparation of α,α,β-trichloropropionic acid according to Berlande's method and found it to melt at 60° and not at 50–52° as he reports. We analyzed the α,α,β-trichloropropionic acid so prepared to prove its purity.

Anal. Calcd. for $C_3H_3O_2Cl_3$: Cl, 60.0. Found: Cl, 60.37, 60.17.

A mixture of the trichloropropionic acid obtained from the ozonization of chlorovinylacrylic acid dichloride with the synthesized α,α,β-trichloropropionic acid also melted at 60°. It was observed that the acid is very hygroscopic and if allowed to stand in a moist atmosphere for a short time the melting point is materially lowered. This proves beyond any doubt that chlorovinylacrylic acid dichloride has the structure $CH_2ClCCl_2CH{=}CHCOOH$, and therefore the chlorovinylacrylic acid has the structure $CH_2{=}CClCH{=}CHCOOH$.

Summary

1. By chlorination of vinylacrylic acid a dichloride is formed whose structure was proved by ozonization to be a 3,4-derivative and not a 1,4-derivative as required by Thiele's theory of addition to conjugated systems.

2. 3,4-Dichloro-Δ^1-pentenic acid loses a molecule of hydrogen chloride to give 3-chlorovinylacrylic acid.

3. 3-Chlorovinylacrylic acid absorbs one molecule of chlorine in the 3,4-position to give 3,3′,4-trichloro-Δ^1-pentenic acid. Its structure was proved by ozonization.

4. On distilling 3,4-dichloro-Δ^1-pentenic acid two molecules of hydrogen chloride are lost and a γ-lactone, $CH_2{=}CCH{=}CHC{=}O$ (with O bridging the ends) is formed.

5. The melting point of α,α,β-trichloropropionic acid is corrected.

6. An electronic structure for conjugated systems is suggested.

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[CONTRIBUTION FROM THE JOHNS HOPKINS UNIVERSITY AND THE BUREAU OF CHEMISTRY AND SOILS]

PHENACYL, PARA-CHLOROPHENACYL AND PARA-BROMOPHENACYL ESTERS OF SOME HIGHER FATTY ACIDS

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The utilization of phenacyl and para halogen phenacyl esters for the identification and separation of acids has been indicated by Rather and Reid[1] and by Judefind and Reid.[2] The successful employment of these reagents for fruit acids has suggested the possibility of quantitative differentiation of the fatty acids obtained from the saponification of the glycerides contained in fats and vegetable oils. The present accepted analytical procedure for substances of this nature consists in esterify-

[9] Berlande, *Bull. soc. chim.*, [4] **37**, 1385 (1925).

[1] Rather and Reid, THIS JOURNAL, **41**, 75 (1919).

[2] Judefind and Reid, *ibid.*, **42**, 1043 (1920).

ing the acids obtained upon saponification, followed by repeated fractionation in vacuo, resaponification and recovery and identification of the free acids. This process, while quantitatively exact, is time consuming and requires close attention and care for its successful completion.

Unfortunately the solubilities of the phenacyl and halogen phenacyl esters of the higher fatty acids are of such an order as to preclude their use in this regard. They are, however, beautiful crystalline compounds which are of value for the establishment of the identity of the higher members of the fatty acid series.

Experimental

The acetophenones and phenacyl bromides were prepared in accordance with the directions of Judefind and Reid. In the preparation of *p*-chloro-acetophenone an appreciable quantity of *p*-chlorobenzoic acid was isolated as a secondary reaction product. In brominating *p*-chloro-acetophenone, it was found convenient to dissolve it in twice its weight of glacial acetic acid, add exactly one molecular quantity of bromine, heat gently to decolorization and cool in ice. Pure ω-bromo-*p*-chloro-acetophenone then separated in brilliant plates in quantitative yield.

The general method of procedure adopted for the preparation of the esters was as follows. One gram of acid was weighed out, an amount of normal sodium hydroxide almost sufficient to neutralize the acid was added, and the mixture was boiled with 10 cc. of 95% alcohol until acid to phenolphthalein. An excess of acid is essential to prevent formation of the corresponding phenacyl alcohol, which would contaminate the crystal-

TABLE I

PROPERTIES OF ESTERS OF SOME HIGHER FATTY ACIDS

Ester of	M. p., °C.	Appearance	Soly., g. in 100 cc. of 95% EtOH 20°	25°
		Phenacyl Esters		
Lauric	48–49	Long, soft acicular needles	2.9150	5.3800
Myristic	56	Soft fluffy plates	1.6980	1.7490
Palmitic	63	Brilliant flat scales	0.5136	0.7890
Stearic	69	Dull cottony needles	.2160	.3650
Arachidic	85–86	Soft white powder	.1348	.2660
Lignoceric	87–88	Soft white powder	.1204	.1816
		p-Chlorophenacyl Esters		
Lauric	70	Brilliant scales	0.6060	0.7856
Myristic	76	Brilliant glistening scales	.2472	.3071
Palmitic	82	Brilliant soft needles	.0784	.1020
Stearic	86	Microcrystalline felted needles	.0648	.1000
Arachidic	86	Microcrystalline aggregates	.0100	.0125
Lignoceric	99–100	Microcrystalline powder	.0054	.0072
		p-Bromophenacyl Esters		
Lauric	76	Brilliant scales	0.3832	0.4288
Myristic	81	Brilliant platelets	.1600	.2092
Palmitic	86	Brilliant scales	.0512	.0684
Stearic	90	Brilliant platelets	.0200	.0260
Arachidic	89	Dull microcrystalline aggregates	.0080	.0096
Lignoceric	90–91	Dull microcrystalline powder	.0040	.0072

line fatty acid ester. A molecular proportion of the desired phenacyl or halogen phenacyl bromide was then introduced, and the reaction mixture boiled under a reflux condenser with the addition of sufficient alcohol to keep the reaction product in solution. After being heated for one hour, the flask was cooled, and the separated solid recrystallized from dilute alcohol to constant melting point. Analysis for halogen by the Parr bomb proved the compounds to be the expected esters.

All the phenacyl compounds prepared are colorless crystalline solids, the majority of them exhibiting a marked luster. This property decreases with increase in molecular weight, and a tendency is noted toward decrease in crystal size with increase in molecular weight.

Approximate solubility determinations were made by removing a 25-cc. portion of the saturated solution from solutions maintained at 20 and 25° in suitable constant temperature baths and drying to constant weight.

The data which have been accumulated are included in Table I.

Summary

Phenacyl, *p*-chlorophenacyl and *p*-bromophenacyl esters of lauric, myristic, palmitic, stearic, arachidic and lignoceric acids have been prepared and described.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

AMMONOLYSIS OF KETONES

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In general the ammono ketones[1] have been prepared by the action of ammonia or substituted ammonia on ketones or dihalogen compounds of the formula R_2CX_2, where X represents halogen,[2] and by the reaction of Grignard reagents and the nitriles.[3]

Since the reaction of ammonia with ketones is obviously a reversible

[1] For a discussion of the terms and methods used in this paper see Strain, THIS JOURNAL, **49**, 1558 (1927), and the included references to Franklin and his co-workers.

[2] Pauly, *Ann.*, **187**, 199 (1877); Thomae, *Arch. Pharm.*, **243**, 395 (1905); Hantzsch and Kraft, *Ber.*, **24**, 3516 (1891).

[3] Moureu and Mignonac, *Compt. rend.*, **156**, 1801 (1913); *ibid.*, **158**, 1395 (1914). Of the three types of ammono ketones which are theoretically possible, only those corresponding to the aldimines and to the ammono aldehyde-acetals are known [Strain, THIS JOURNAL, **50**, 2218 (1928)].

$R_2C{=}NH$	$R_2C{=}NR$	$(R_2C{=}N)_2{>}CR_2$ (unknown)
Ketimine (known)	Ketimine (known)	

Attempts to prepare the ammono ketones analogous to the hydramides have resulted in the formation of ketisoketimines or other products [Moureu and Mignonac]. Although Thomae [*Archiv. Pharm.*, **243**, 373 (1905); *ibid.*, **244**, 641 (1906); *ibid.*, **246**, 373 (1908)] claims to have prepared an ammono ketone analogous to the hydramides by the action of ammonia on ethyl methyl ketone, his work has been questioned by Traube [*Ber.*, **41**, 777 (1908); *ibid.*, **42**, 3298 (1909)], who could not duplicate the results.