used as reference materials and solutions of ethanol in water as media. Errors due to variation in temperature have been analyzed for the systems and apparatus employed.

Acknowledgments

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Acetin Fats. I. Products Made from Mixed Acetin Fats

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THE introduction of acetyl groups into glyceride molecules results in the formation of fats with interesting and unusual properties (1-5). These properties permit the designing of products that are either improved versions of existing types or represent new materials. The present report deals with fats which contain both the possible types of mixed acetyl glycerides, namely, mono- and diacetyl triglycerides, beside the normal triglycerides. The terms "monoacetins" and "diacetins," respectively, are used in this paper for these monoacetyl and diacetyl triglycerides. The general term "acetin fats" is proposed for these mixed acetyl glycerides regardless of melting point. The preparation and use of acetin fats containing predominantly oleic as the high molecular weight fatty acid have been described by Feuge *et al.* (6).

The most useful effect of the introduction of acetyl groups into glyceride molecules is the pronounced lowering of the melting point. Heretofore the use of a low melting fat called for an unhydrogenated or only slightly hydrogenated oil. Such highly unsaturated oils, *e.g.*, cottonseed or soybean oil, do not have the oxygen stability or keeping quality of partially hydrogenated oils, a fact which has limited their current use in the production of plastic shortenings. Existing commercial shortenings are made principally from a partially hydrogenated oil or basestock which is stiffened by the addition of a low I.V. hydrogenated fat or hardstock to give the so-called all-hydrogenated type shortening. Improved techniques of hydrogenation and plasticizing have significantly improved the overall plasticity of these products, but they still do not approach the plastic range of the so-called compound or blended type shortenings which consist of hardstock in oil and which show relatively little change in plasticity from a refrigerator temperature of between 40° to 50°F. to a room temperature of up to about 100°F. The aim of equal or increased oxygen stability and wider plastic range, in comparison with conventional shortenings, was accomplished in plastic fats made from acetin fat basestocks by virtue of the lower melting points of the component acetyl glycerides. As an illustration of the potentialities of this new type of fat, the properties of acetin fat shortenings will be described.

Preparation of Acetin Fats

The mixed acetin fats may be prepared by a number of methods. The two methods most often employed involve interesterification of normal fats and oils with triacetin or acetylation of a superglycerinated fat. In the first method a low-temperature interesterification catalyst is added to a mixture of triacetin and conventional triglycerides composed of fatty acids of the desired molecular weight range and degree of unsaturation. The usual refining, bleaching, and deodorization steps as well as inactivation of the catalyst must be instituted somewhere in the processing. Deodorization of acetin fats yields a bland product and removes the small quantity of triacetin present. A more detailed description of a preparation is given below.

To a refined and dried or deodorized oil or fat in the liquid state is added the selected quantity of triacetin. The amount of triacetin[1] is chosen on the basis of the content of acetyl groups desired in the final interesterification product. To the mixture of oil or melted fat and triacetin is added about 0.3% of a low-temperature interesterification catalyst, such as sodium methoxide or sodium metal, as a suspension in an inert solvent such as xylene. With agitation the two-phase mixture rapidly becomes homogeneous as

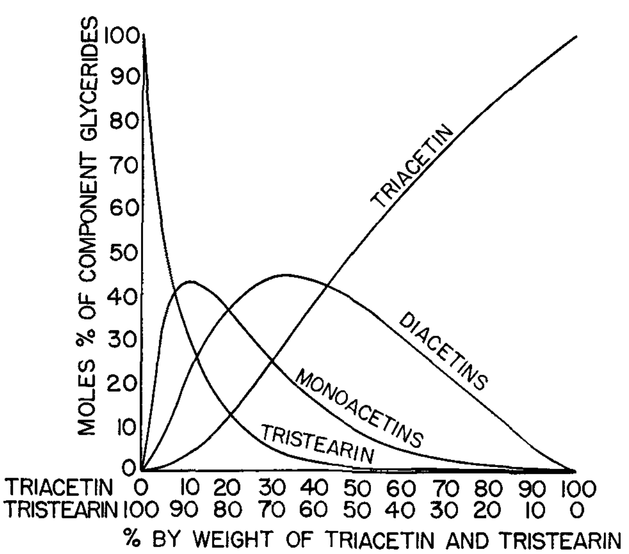

Fig. 1. Composition of component glycerides at equilibrium of interesterified tristearin-triacetin, mixes, calculated in moles %.

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[1] Figures 1 and 2 express the molar and weight concentrations of the various triglycerides present after random interesterification of triacetin and tristearin. Figure 3 shows the weight percentage concentrations of the component glycerides in the triacetin-free fats.

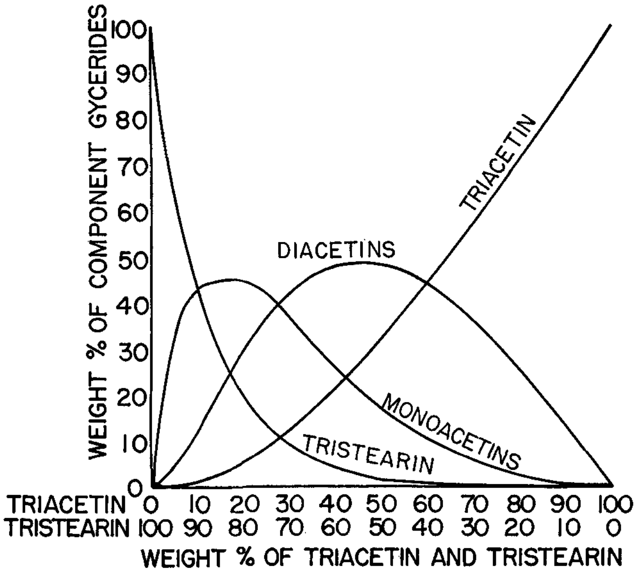

FIG. 2. Composition of component glycerides at equilibrium of interesterified tristearin-triacetin mixes, calculated in weight %.

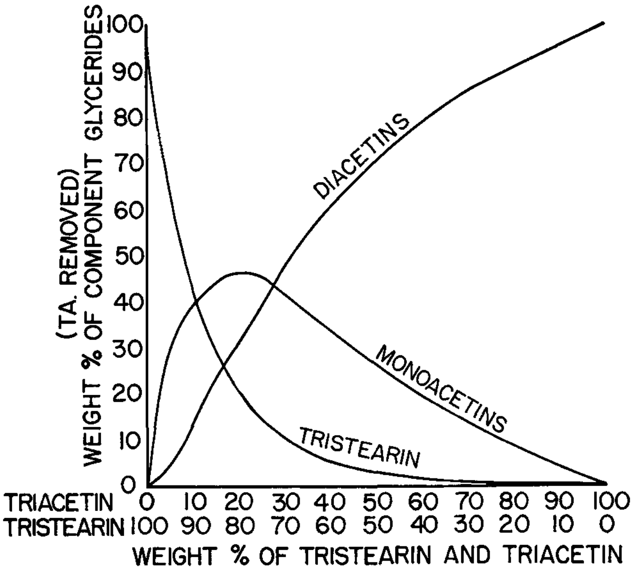

FIG. 3. Composition, in weight %, of triacetin-free randomly interesterified tristearin-triacetin mixes.

interesterification occurs. The interesterified mix is maintained at about 100°F., or higher if necessary to maintain a homogeneous mix. Within about one-half hour random interesterification is complete. The interesterification catalyst is inactivated by acidulation or water-washing. If acidulation is employed, the excess acid is removed by a refining or water-washing step. Water-washing removes a substantial portion of the triacetin present. This may be avoided by use of a dry-refining process. Usually it is desirable to remove all triacetin from the acetin fat. This may be accomplished by deodorization. Normal deodorization conditions serve to prepare a bland product as well as remove any triacetin present which may be undesirable from a performance standpoint. Too high a temperature or too low a pressure or a combination thereof during deodorization is to be avoided as partial distillation of diacetyl triglycerides may occur. The resulting acetin fat may be used as a salad oil, margarine oil, etc., or compounded with a higher melting glyceride to give shortenings, margarines, or similar products.

Melting Behavior of Acetin Fats

The data in Table I indicate the degree to which melting points of partially hydrogenated fats may be lowered by the introduction of acetyl groups. A reduction in complete melting point of 25-35° F. is obtained when the original fat has a melting point above about 90°F. This reduction is gained, of course, with equivalent or superior keeping quality.

The properties of fats both performance-wise and nutritionally are much more closely allied to the solid contents or percentage of solids in the fat over a temperature range than to melting point. A relative expression of solids contents can be obtained by dilatometric examination. Figure 4 presents SCI (solid content index) data on three acetin fats made from hydrogenated soybean oil of I.V. 51 whose melting behavior is shown in Table I. The overall change in solids is quite marked and serves to illustrate why the performance differences of these fats are so striking.

Plasticity of Acetin Fat Shortenings

Both the compound or blended and the all-hydrogenated type shortenings can be made from acetin fats by adding hard fat and plasticizing in an accepted manner. In each instance the acetin fat shortenings have a marked superiority in keeping quality. The shortening type obtained is determined by the melting behavior of the base stock used. For a compound type shortening an acetin oil or liquid acetin fat is used. For the all-hydrogenated type an acetin fat is chosen which exhibits some change in solids over the practical temperature range. In each case

TABLE I

Melting Behavior of Some Acetin Fats of Various Iodine Values and Acetic Acid Contents

	Original Oil or Fat			Acetin Fat							
	I.V.	Cmp.		%Acetic Acid[a]	I.V.	Inc.[c] M.P.		Cmp.		SCI[b] 70°F.	SCI 92°F.
		°C.	(°F.)			°C.	(°F.)	°C.	(°F.)		
Soybean Oil	133	8.9	(48.0)	15.5	109.0	−25	(−13)	−6.0	(21.2)	......	......
Cottonseed Oil	110	9.5	(49.1)	15.5	88.3	−10	(+14)	2.0	(35.6)	......	......
Coconut Oil	9	25.2	(77.4)	16.9	7.2	−12	(+10)	12.0	(53.6)	......	......
Hydrogenated Soybean Oil	51	54.0	(129.2)	11.4	44.1	27.2	(81.0)	43.6	(110.5)	29.2	11.0
Hydrogenated Soybean Oil	51	54.0	(129.2)	15.4	42.4	35.0	(95.0)	40.9	(105.6)	27.1	9.5
Hydrogenated Soybean Oil	51	54.0	(129.2)	17.9	40.2	17.7	(63.9)	34.4	(93.9)	5.8	3.3
Hydrogenated Cottonseed Oil	42	50.8	(123.4)	13.0	36.8	26.9	(80.4)	36.8	(98.2)	16.9	3.8

[a] Values calculated from the quantities of triacetin and normal fat used in the interesterification assuming random interesterification and a triacetin-free product.
[b] Solid content index.
[c] Incipient.

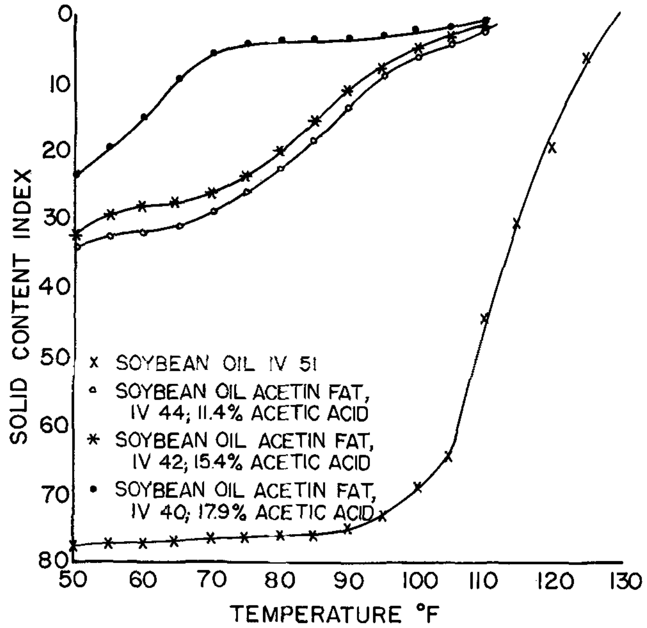

FIG. 4. Dilatometric curves of some soybean oil IV 51 acetin fat basestocks.

the melting behavior is controlled by proper selection of the molecular weight and degree of saturation of the component high-molecular-weight acids and by the amount of acetic acid introduced into the acetin fats. Acetin fats yielding essentially a compound type shortening upon formulation may be made from animal or vegetable fats of C_{16} to C_{18} fatty acid composition whose iodine values are as low as 55-60. All-hydrogenated type shortenings may be made from C_{16} to C_{18} fats whose iodine values are as low as 40. It is obvious that the high degree of saturation or hydrogenation that can be tolerated in acetin basestocks eliminates keeping quality as a problem with this type of shortening.

Table II illustrates the different types of shortening that can be prepared from acetin fats. The relative plasticity of the shortenings was measured by use of an A.S.T.M. grease penetrometer-200-g. needle weight. The first shortening listed, made from hydrogenated cottonseed oil (CSO) of I.V. 74 and 6% CSO I.V. 8, may be regarded as similar to the all-hydrogenated commercial type. The last shortening illustrates how a wide plastic range acetin fat shortening can be prepared without the addition of hard fat by simply forming the hard fat *in situ* by directed interesterification.

Figure 5 shows more clearly the change in plasticity with change in temperature, again as measured by the A.S.T.M. penetrometer. It is noted that the plasticity of the control shortening made from CSO I.V. 8 in CSO I.V. 74 is inferior to the acetin product made from CSO I.V. 74. The wide plastic range of the acetin fat product is simply a reflection of the fact that the base stock is contributing little to the change in solids over the temperature range.

Texture of Acetin Fat Shortenings

Fresh acetin fat shortenings, particularly those made from partially hydrogenated oils of I.V. about 70-80, have textures equal to or superior to normal all-hydrogenated type shortenings. Texture differences between normal fats and acetin fat shortenings become more pronounced upon aging. Much less firming was encountered in the acetin shortenings after two months' storage at 50-100°F. In most instances the acetin fat shortenings remained soft and pliable whereas normal commercial type shortenings became dry and ribby. Firming in commercial shortenings is particularly pronounced when the shortening has been exposed to relatively high temperatures, that is, about 120°F. The so-called heat damage to the shortening caused by such exposure is seen when the shortening is returned to normal storage temperature, about 70°F. The commercial shortening then is dry, ribby, and very firm. Its plasticity as measured by depth of penetration is decreased by one-half. Acetin fat shortenings, particularly of the compound type, are less soupy at the high temperature and show considerably less firming on returning to normal temperature. Hence they are extremely resistant to heat damage.

Flavor of Acetin Fats

Flavor stability testing on acetin fats has been somewhat limited. However neither in shortenings nor liquid base stocks stored at temperatures up to 100°F. for one month has any evidence of acetic acid odor or flavor been observed. Flavor development appears to be typical of the original base oil or fat.

TABLE II

Consistency of Some Acetin Fat Shortenings as Illustrated by Penetration Data[a]

Normal Basestock	Weight Ratio-Triacetin: Normal Basestock —used in the Interesterification	I.V. of Acetin Basestock	Hardstock (Hard Fat)	% Acetic Acid in Shortening	Penetration at				
					50°F.	60°F.	70°F.	80°F.	90°F.
Cottonseed Oil IV74	......	....	6% Cottonseed Oil IV8	0	108	139	213	270	395
Cottonseed Oil IV74	1:5	64	11% Cottonseed Oil IV8	10.1	197	213	233	245	228
Cottonseed Oil IV74	1:2	58	12% Cottonseed Oil IV8	15.8	204	209	220	220	......
Cottonseed Oil IV74	1:5	64	15% Lard IV5	9.7	215	209	243	231	260
Soybean Oil IV73	......	....	4.5% Cottonseed Oil IV8	0	63	88	135	160	247
Soybean Oil IV73	1:5	63	13% Cottonseed Oil IV8	9.9	191	214	222	228	......
Cottonseed Oil IV62	......	62	3% Cottonseed Oil IV8	0	54	64	90	125	188
Cottonseed Oil IV62	1:2	49	12% Cottonseed Oil IV8	15.8	203	216	245	247	223
Cottonseed Oil IV51	......	....	None	0	19	20	39	30	33
Cottonseed Oil IV51	1:5	44	10% Cottonseed Oil IV8	10.3	97	121	197	240	285
Cottonseed Oil IV51	1:2	42	9.5% Cottonseed Oil IV8	16.2	151	161	208	248	281
Cottonseed Oil IV74	1:5	64	None—directed interesterified (7)	11.4	151	164	176	211	293

[a] A.S.T.M. grease penetrometer—200-g. needle weight. Values presented represent depth of penetration in mms./10.

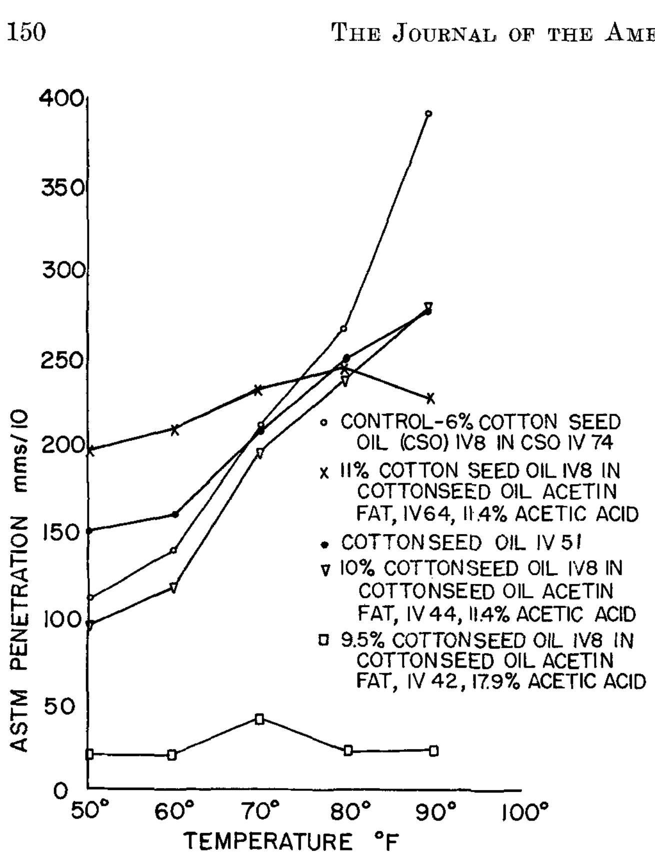

FIG. 5. Consistency data on some acetin fat shortenings as measured by an ASTM grease penetrometer—200 gram needle weight.

Performance of Acetin Fat Shortenings

The performance of these shortenings, as far as flavor, odor development, and texture are concerned, has been mentioned. With regard to baking performance, workability, creaming volume, and gum and foam formation the acetin fat shortenings are equivalent to or better than the control commercial shortenings. Typical data are given in Table III obtained from the shortening prepared from CSO I.V. 74. The single exception to comparable or superior performance to control shortenings is in a lower smoke point. Acetin fats without exception smoke at about 300°F. This somewhat low smoke point is caused by the higher volatility of component diacetyl triglycerides. If desired, these can be removed by distillation. The resulting acetin fats which are composed of normal triglycerides and monoacetyl triglycerides have a smoke point of about 400°F. They retain however a substantial portion of the beneficial lowering of melting point due to the acetyl content.

TABLE III

Performance Comparison of an Acetin Fat Shortening with a Control (All-Hydrogenated Type) Shortening

	Acetin Fat Shortening	Control Shortening
White cake vol. cc./lb. (4½% of a commercial superglycerinated fat added)	1,200	1,170
Creaming, volume—% air incorporated during creaming	163	160
Foam—produced under deep-fat frying conditions	1/16"	¼"
Smoke point, °F	305	420

Discussion

The general utility of acetin fats lies in the fact that introduction of acetic acid into the glyceride molecule lowers the melting point. This means that oils can be hydrogenated to a lower I.V. than formerly, thus increasing the stability of a product against oxidation. It also means that unhydrogenated oils or fats which are normally too hard to use as base stocks and the like can now be utilized. In this category tallow is outstanding.

In general, the mixed acetin fats can be substituted for or replace normal triglyceride fats in any edible fat use, provided the smoke point limitation is kept in mind. A low smoke point is not a problem if, as has been mentioned, the component diacetyl triglycerides are removed. The actual extent to which acetin fats could replace normal fats can be determined only by extensive investigation. However a number of potential uses appears definite. The use of acetin fats in the preparation of compound and all-hydrogenated shortenings has been described. The compound type shortening is adaptable to serve as a spread useful under extreme climatic conditions.

These mixed acetin fats may also be utilized in the second largest edible fat usage, *i.e.*, as a spread. The primary qualification of a good margarine fat is an equitable balance between two diametrically opposed requirements, *i.e.*, the margarine must be sufficiently low melting to melt substantially at body temperature, yet sufficiently high melting to have adequate heat resistance. Margarine oils satisfying this qualification can be produced from partially hydrogenated acetin fats of exceptionally low I.V. and hence good oxidative keeping quality. Table I presented data on an oil from CSO I.V. 42 interesterified with triacetin that has the desired complete melting behavior. The second main qualification of a margarine fat is spreadability. Spreadability is exemplified by little change in plasticity over the practical temperature range of 40-100°F. The acetin fat mentioned above is at least equal to the best of commercial margarine oils in spreadability.

Essentially two approaches can be applied to acetin fats to render them superior to normal margarine oils in spreadability. The first approach is to apply the interesterification process in such a manner that the number of mixed glycerides composed solely of high-molecular-weight saturated and isooleic acids is increased. The composition of these intermediate melting glycerides can be so selected as to give a product which shows little change in solids until about 100° F., at which point melting is quite sharp. The second and a similar approach would be to add from an outside source the proper intermediate-melting glyceride directly to the selected acetin oil.

Acetin salad oils can be prepared directly from vegetable oils. For example cottonseed oil cannot be used as a salad oil without winterizing. An acetin fat made from CSO containing 21.9% acetic acid shows sufficient chill test stability at 40°F. to suggest its use as a comparatively oxygen-stable salad oil. Similarly coconut oil or hydrogenated coconut oil can be be made into a salad oil. Removal of the component diacetins from the salad oils yields frying or cooking oils of improved keeping qualities.

In many instances mixed acetin fats may be substituted for normal fats when improved keeping quality is desired. In some instances they can replace existing normal fat products and perform better in a certain usage or even permit a new use. To illustrate this point, attention is directed to the fact that mixed acetin fats yield wide plastic range products of a keeping quality heretofore unknown. Utility in many other edible fat products will no doubt become apparent as the fats are investigated further.

The unique properties of mixed acetin fats also suggest many potential applications to inedible uses. Some of the more promising ones include plasticizers for various polymers, a replacement for palm oil in tinning, and as hydraulic oils.

Summary

The most striking effect of the introduction of the acetyl group into the glyceride molecule is the reduction in melting point. This effect permits the preparation of low melting fats and oils, or acetin fats, of a high degree of saturation and of a significantly increased oxidative keeping quality.

Mixed acetin fats containing monoacetyl (monoacetins), diacetyl (diacetins), and normal triglycerides were made by random interesterification of normal fats or oils with triacetin, followed by removal of the residual triacetin.

In general, mixed acetin fats may replace normal triglycerides in any edible fat use. Edible fat products including shortenings, margarines, or spreads, salad oils, and frying oils were made from acetin fats and oils.

Suggested inedible use applications of the acetin fats and oils include plasticizers, tinning oils, and hydraulic oils.

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Reactions of Fatty Acid Chlorides. I. Preparation of Fatty Acid Anhydrides

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DURING the course of a program of research on chemical utilization of fatty acid chlorides it became evident that although there have been reported a variety of synthetic methods, there does not exist a systematic survey of the preparation of the anhydrides of the higher fatty acids. This communication deals with an investigation of various syntheses including a newer one employing fatty acid chlorides and the application of the optimum to the preparation of the anhydrides of the fatty acids from decanoic to stearic including oleic. Furthermore there are presented revised and new physical data determined by modern techniques on materials of unambiguous purity.

Aliphatic acid anhydrides have been prepared almost exclusively from either the alkali or silver salts of acids and the corresponding acid chlorides, (B), (23, 37, 41, 44); from certain acids and acetic anhydride, (C), (18, 19, 26, 28, 43); from the acid chloride, corresponding acid and pyridine, (D), (4) or from the acid chloride-pyridine adduct and water, (E), (2):

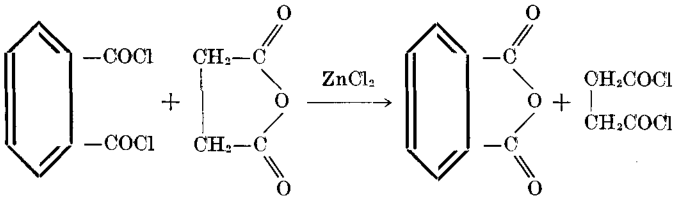
$$\text{(B)}\ RCOCl + RCOOM \longrightarrow (RCO)_2O + MCl$$

$$\text{(C)}\ 2RCOOH + (CH_3CO)_2O \longrightarrow (RCO)_2O + 2CH_3COOH$$

$$\text{(D)}\ RCOCl + RCOOH + C_5H_5N \longrightarrow (RCO)_2O + C_5H_5NHCl$$

$$\text{(E)}\ 2RCOC_5H_5NCl + H_2O \longrightarrow (RCO)_2O + 2C_5H_5NHCl$$

The suggestion of Zetzsche (45) that anhydrides could be easily prepared from the acid chloride and acetic anhydride, based upon his observation that benzoic anhydride could be obtained from benzoyl chloride and acetic anhydride, has apparently never been applied to aliphatic acid anhydrides. In the aromatic series the conversion of phthaloyl chloride to phthalic anhydride with maleic or succinic anhydrides at 140-200° in the presence of zinc chloride has been reported by Kyrides (24):



Acetyl chloride has been used to convert efficiently dicarboxylic acids such as glutaric, adipic, and sebacic acids to anhydrides (12, 27, 42). Yields of 55-75% of acid anhydrides have also been claimed by heating the acid to 120-125°, adding excess acetyl chloride dropwise, heating to 180°, and fractionating the products under vacuum (13). These reactions may be postulated as proceeding in three ways based upon known experimental evidence.

$$\begin{array}{ll}
\text{(I)} & 2RCOOH \rightleftharpoons (RCO)_2O + H_2O \\
 & R'COCl + H_2O \rightleftharpoons R'COOH + HCl \\ \hline
 & 2RCOOH + R'COCl \rightleftharpoons (RCO)_2O + R'COOH + HCl \\
\text{(II)} & 2RCOOH \rightleftharpoons (RCO)_2O + H_2O \\
 & 2R'COCl + H_2O \rightleftharpoons (R'CO)_2O + 2HCl \\ \hline
 & 2RCOOH + 2R'COCl \rightleftharpoons (RCO)_2O + (R'CO)_2O + 2HCl \\
\text{(III)} & 2RCOOH + 2R'COCl \rightleftharpoons 2RCOOCOR' + 2HCl \\
 & 2RCOOCOR' \rightleftharpoons (RCO)_2O + (R'CO)_2O \\ \hline
 & 2RCOOH + 2R'COCl \rightleftharpoons (RCO)_2O + (R'CO)_2O + 2HCl
\end{array}$$