chloric acid. The aqueous solution was then extracted with ether and steam distilled for some time. At this point sodium hydroxide was added in excess and the α-phenyltetrahydropyridine was removed by steam distillation. Extraction of the distillate gave a 48% yield of the compound, which was characterized by its hydrochloride (m. p. 86–87°), picrate (m. p. 180–181°) and chloroplatinate, as described by Gabriel.[7]

α-Phenyltetrahydropyridine chloroplatinate was precipitated from an alcoholic solution of the hydrochloride by the addition of alcoholic chloroplatinic acid. According to Gabriel the compound sinters at about 190°, foams at 191–192°, then resolidifies, softens again and gives an almost clear red-brown melt at 202°. In the case of our compound the final melting did not appear to take place until 210–211°.

Anal. Calcd. for $C_{22}H_{28}N_2Cl_6Pt$: Pt, 26.80. Found: Pt, 26.52, 26.97.

Summary

A method has been described for the synthesis of α-phenyltetrahydropyridine by the action of phenylmagnesium bromide on δ-bromovaleronitrile, which may be obtained by the action of potassium cyanide on 1,4-dibromobutane. The latter compound may be prepared by the action of phosphorus pentabromide on tetrahydrofuran, which, in turn, may be obtained by the hydrogenation of furan, in the presence of Raney catalytic nickel.

Other communications will follow on the synthesis of other α-, α,β-, etc., substituted tetrahydropyridines, their hydrogenation products and related derivatives.

TROY, N. Y. RECEIVED JULY 14, 1934

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[7] Gabriel, *Ber.*, **41**, 2010 (1908).

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, NO. 139]

The Action of Phosphorus Pentahalides and Thionyl Chloride on Some Saturated and Unsaturated 1,4-Diketones and 2,5-Diphenylfurans

BY ROBERT E. LUTZ AND FRANK N. WILDER

The action of phosphorus pentachloride on various saturated and unsaturated 1,4-diketones and diphenylfurans has been mentioned in previous communications, and it is the object of this report to collect, extend and correlate the data. The end-product of most of these reactions is the known 2,5-diphenyl-3,4-dichlorofuran (II).[1]

Hydrogens or acetoxy groups in the beta positions in the diphenylfurans are easily replaced by halogens on short heating with phosphorus pentahalides. Diphenylfuran (I) reacts with phosphorus pentachloride at 25–40° giving the monochlorofuran III which under more drastic conditions at 100° is converted into the dichlorofuran II. Diphenylacetoxyfuran V reacts at 25–40° through replacement of the one beta hydrogen with chlorine giving the chloroacetoxyfuran VI; the acetoxy group of the latter is itself replaced with chlorine under more drastic conditions at 100°. The acetoxy groups of 2,5-diphenyldiacetoxyfuran IV are also replaceable, stepwise; the first may be replaced by means of acetyl chloride and sulfuric acid.[2] These reactions are illustrated in Diagram 1.

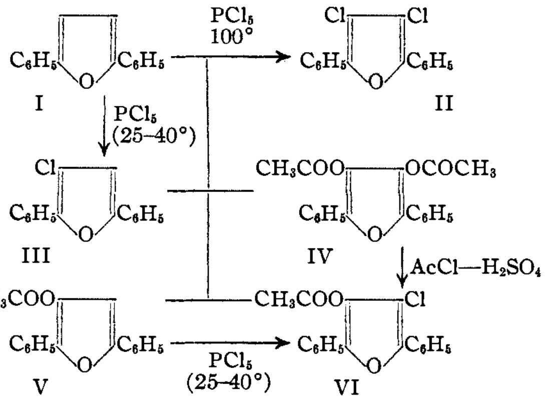

DIAGRAM 1.

The replacement of aromatic hydrogen with halogen by means of phosphorus pentachloride is not a common reaction; it has been accomplished in the case of anisole.[3] The substitution in the furan series occurs with great ease, even in the absence of activating substituents such as methoxyl, hydroxyl and acetoxy. The furan nucleus is therefore to some extent comparable in activity with the benzene nucleus of anisole, a phenomenon in accord with the so-called super-aromatic character of the furan nucleus.[4] The reactions

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[1] *Cf.* (a) Conant and Lutz, THIS JOURNAL, **47**, 881 (1925); (b) Lutz and Wilder, *ibid.*, **56**, 978 (1934).

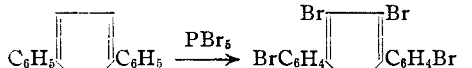
[2] Lutz and Wilder, *ibid.*, **56**, (a) 1980, (b) 1987 (1934).

[3] Henry, *Ber.*, **2**, 711 (1869); Hayashi, *J. prakt. Chem.*, **123**, 306 (1929).

[4] *Cf.* Gilman and Towne, *Rec. trav. chem.*, **51**, 1054 (1932); Gilman and Calloway, THIS JOURNAL, **55**, 4197 (1933); Gilman and Young, *ibid.*, **56**, 464 (1934).

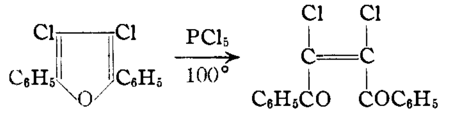
are probably best interpreted in terms of addition and elimination.[5]

Two typical furans, namely, diphenylfuran and diphenylacetoxyfuran, were found to react with phosphorus pentabromide, giving in both cases the known 2,5-di-(*p*-bromophenyl)-3,4-dibromofuran[6] VII. The reactions involve bromination of the α-phenyl groups in the para positions, as well as replacement of the β-hydrogens and acetoxy group in the furan nucleus.



VII

It is noteworthy that diphenyldichlorofuran, the end-product of the phosphorus pentachloride reactions, is itself acted upon by an excess of the reagent on longer heating at 100° to give *cis* dibenzoyldichloroethylene VIII, the product of an oxidation (the *trans* dibenzoyldichloroethylene is stable under these conditions).



VIII

This reaction is closely analogous to the nitric-glacial acetic acid oxidations of furans to *cis* unsaturated 1,4-diketones,[1b] and probably involves a similar mechanism, namely, the 1,4-addition of the reagent (or of chlorine) to the furan nucleus, generating the double bond before the opening of the furan ring, followed by hydrolysis and the formation of the highly conjugated unsaturated 1,4-diketone system.

The characteristic dehydration of saturated 1,4-diketones to furans is possible through the action of phosphorus pentachloride, but chlorination usually results also. Some illustrations are given in Diagram 2. Dibenzoylchloroethane X gives diphenyldichlorofuran when heated with the reagent at 100° but does not react at room temperature. Dibenzoylethylene oxide XII reacts similarly at 100° while the chlorohydrin XI reacts readily at room temperature.[2b] The dibenzoyldihalogenoethanes fail to react at 100°,[2b] and at higher temperatures give new products which have not yet been studied. Dibenzoylethane IX reacts only when heated, giving the monochlorofuran, the second chlorine being introduced under the more prolonged action of the reagent.

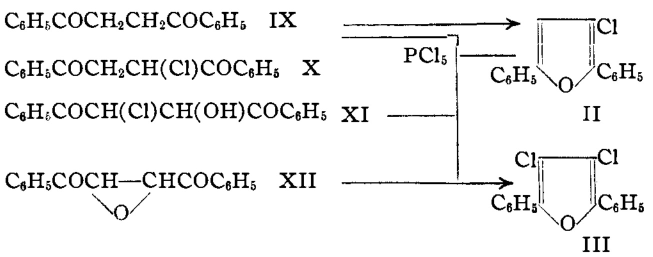


DIAGRAM 2.

Phosphorus pentabromide converts dibenzoylethane into 2,5-di-(*p*-bromophenyl)-3,4-dibromofuran VII.

In the reactions cited in Diagram 2 phosphorus pentachloride causes not only dehydration but partial or complete chlorination as well. Since the *dl*- and *meso*-dibenzoyldichloroethanes are stable under the conditions involved, it is clear that phosphorus pentachloride does not chlorinate directly the alpha positions in the open-chain diketones, and that the furan ring closure takes place first, with subsequent halogenation of any available beta positions.

Various of the unsaturated 1,4-diketones react with phosphorus pentachloride, generally with great readiness at room temperature, to give halogenated furans (see Diagram 3). *Cis* and *trans* dibenzoylethylenes XIII give the monochlorofuran. *Cis* dibenzoylchloroethylene XIV[2] and dibenzoylmethoxy and hydroxyethylenes (XVI and XV) react also at room temperature and are converted directly into the dichlorofuran. *Trans*-dibenzoylchloroethylene reacts similarly but requires heating with the reagent and differs in this respect from the *cis* isomer which reacts easily at room temperature. The reactions with these unsaturated 1,4-diketones proceed with distinctly greater ease than those with the similar saturated diketones, even including the unsubstituted dibenzoylethane itself; the conjugated system is therefore more reactive toward the reagent than the carbonyl group of the saturated 1,4-diketones.

It is noteworthy that the methyl and ethyl enol ethers, the 1,4-diphenyl-4-alkoxy-3-butene-1,2-diones XVII, and also 1,4-diphenyl-4-chloro-3-butene-1,2-dione XVIII, react readily with phosphorus pentachloride to give diphenyldichlorofuran.

Phosphorus pentabromide reacts with dibenzoylethylene and dibenzoylmethoxyethylene to

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(5) *Cf.* the analogous chlorination of indene [Bergmann and Bondi, *Ber.*, **63**, 1159, 2307 (1927)].

(6) Thiele and Rosner, *Ann.*, **306**, 41 (1899); Perkins and Schloesser, *J. Chem. Soc.*, **57**, 947 (1890).

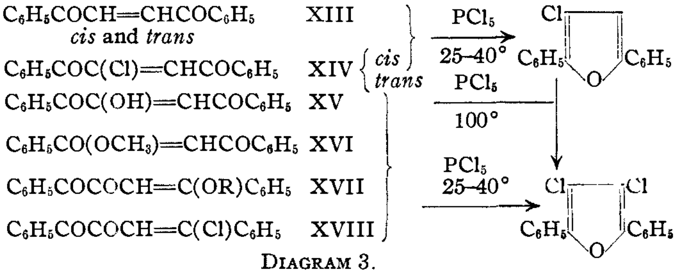
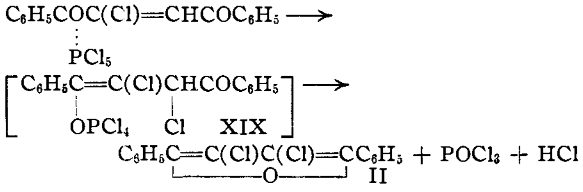


DIAGRAM 3.

give 2,5-di-(*p*-bromophenyl)-3,4-dibromofuran VII.

The mechanism of the reactions between phosphorus pentahalides and the unsaturated 1,4-diketones may best be considered in connection with the action of phosphorus pentachloride on dibenzoylethylene and on the dibenzoylchloroethylenes. The addition of free chlorine from dissociation of phosphorus pentachloride is not involved since this would lead to products incapable of forming the furans under these circumstances. Neither *dl*- nor *meso*-dibenzoyldichloroethanes are acted upon by the reagents and therefore cannot be involved in intermediate steps. The hydrogen chloride generated during the reaction largely escapes and it is unlikely that addition occurs (in the case of the dibenzoylchloroethylene reaction dibenzoyldichloroethane would have been formed to some extent at least[7] and would have been isolated).

The most reasonable interpretation of the reactions appears to us to be the 1,4-addition of phosphorus pentachloride to the conjugated system, as suggested by Straus for the analogous reactions of α,β-unsaturated ketones,[8] followed, however, by the loss of the elements of phosphorus oxychloride and hydrogen chloride with furan ring closure through the remaining carbonyl group, somewhat as follows



$$\mathrm{C_6H_5CO}\underset{\underset{\textstyle\mathrm{PCl_5}}{\vdots}}{}\mathrm{C(Cl){=}CHCOC_6H_5} \longrightarrow$$

$$\left[\mathrm{C_6H_5}\underset{\underset{\textstyle\mathrm{OPCl_4}}{|}}{\mathrm{C}}\mathrm{{=}C(Cl)}\underset{\underset{\textstyle\mathrm{Cl}}{|}}{\mathrm{C}}\mathrm{HCOC_6H_5}\quad \mathrm{XIX}\right] \longrightarrow$$

$$\mathrm{C_6H_5}\underbrace{\mathrm{C{=}C(Cl)C(Cl){=}C}}_{\mathrm{O}}\mathrm{C_6H_5} + \mathrm{POCl_3} + \mathrm{HCl}\qquad \mathrm{II}$$

The mechanism of the final step in the furan ring closure is obscure. It may take place from XIX directly or through loss of phosphorus oxychloride by an α,γ-shift of chlorine from phosphorus to carbon giving

$$\mathrm{C_6H_5}\underset{\underset{\textstyle\mathrm{Cl}}{|}}{\mathrm{C}}\mathrm{{=}C(Cl){-}}\underset{\underset{\textstyle\mathrm{Cl}}{|}}{\mathrm{C}}\mathrm{HCOC_6H_5}$$

XX

The furan ring closure, whether or not it takes place through intermediates such as XIX or XX, may be regarded as analogous to that occurring in the conjugate addition of hydrogen[9] and hydrogen chloride[7] to unsaturated 1,4-diketones where somewhat similar intermediate compounds are assumed.[10]

It is very probable that the mechanism of the action of thionyl chloride on various of the compounds mentioned above is analogous to that of the phosphorus pentahalides. Thionyl chloride at refluxing temperature is without the same degree of chlorinating action, however, since it is without effect on dibenzoylchloro- and dichloroethanes, on diphenylfuran (I) or on diphenyldiacetoxy- and acetoxychlorofurans (IV and VI). The reagent converts dibenzoylhydroxyethane into dibenzoylchloroethane, but dibenzoylethylene oxide and chlorohydrin (XII and XI) are converted into diphenyldichlorofuran.[2b] *Cis*-dibenzoyl ethylene, and also dibenzoylethane, react to give new products the nature of which are not yet clear; *trans*-dibenzoylethylene however gives a non-crystalline product which is converted into dibenzoylchloroethane X when treated with water or ethanol (yield 90%); this probably involves hydrolysis of a primary 1,4-addition product, $\mathrm{C_6H_5C(OSOCl){=}CH{-}CHClCOC_6H_5}$ (XXI). *Trans*-dibenzoylethylene reacts similarly with phosphorus oxychloride, evidently giving an addition compound, possibly $\mathrm{C_6H_5C(OPOCl_2){=}CHCH(Cl)COC_6H_5}$, which on hydrolysis gives dibenzoylchloroethane.

Thionyl chloride is without effect on *trans*-dibenzoylchloroethylene but converts the more active *cis* isomer into diphenyldichlorofuran, a transformation which also may be interpreted in terms of 1,4-addition but with subsequent furan ring closure as in the analogous phosphorus pentachloride reactions, as follows

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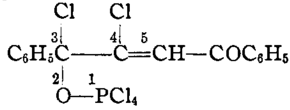
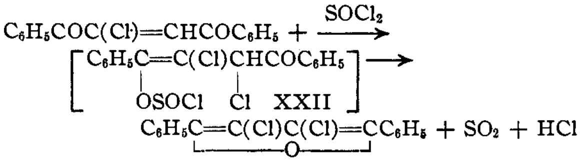
[7] *Cf.* Lutz and Wilder, THIS JOURNAL, **56**, 1193 (1934).

[8] Straus, *Ann.*, **393**, 235 (1912).

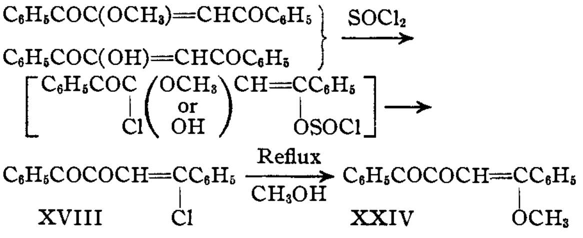
[9] Lutz, THIS JOURNAL, **51**, 3008 (1929); Lutz and Taylor, *ibid.*, **55**, 1595 (1933).

[10] An alternative mechanism is the 1,2-addition of phosphorus pentachloride to one carbonyl group with subsequent rearrangement involving a 1,3- 1,5- or 3,5-shift of chlorine in the hypothetical intermediate  $\mathrm{C_6H_5}\overset{\overset{\textstyle\mathrm{Cl}}{{}^3|}}{\underset{\underset{\textstyle\mathrm{O{-}^1PCl_4}}{{}_2|}}{\mathrm{C}}}\mathrm{{-}}\overset{\overset{\textstyle\mathrm{Cl}}{{}^4|\ {}^5}}{\mathrm{C}}\mathrm{{=}CH{-}COC_6H_5}$, phosphorus oxychloride being eliminated through the 1,3- or 1,5-shift of chlorine. In the case of dibenzoylchloroethylene, however, the carbonyl group which must be presumed to react should be the least likely to do so because of steric hindrance. This is the case also with dibenzoylphenylethylene types which react similarly with great ease (unpublished results). Unless one assumes that both carbonyls undergo reversible additions, this consideration would appear to favor the 1,4-mechanism.



$$C_6H_5COC(Cl){=}CHCOC_6H_5 + \xrightarrow{SOCl_2} \left[\underset{\substack{|\\OSOCl}}{C_6H_5C}{=}\underset{\substack{|\\Cl}}{C(Cl)CH}COC_6H_5 \;\; \text{XXII}\right] \longrightarrow \underbrace{C_6H_5C{=}C(Cl)C(Cl){=}CC_6H_5}_{O} + SO_2 + HCl$$

Thionyl chloride reacts readily with dibenzoylmethoxyethylene and with dibenzoylethenol; the result is the loss of methoxyl (or hydroxyl) and gain of chlorine with the formation in both cases of the same product, which is isomeric with *cis* and *trans* dibenzoylchloroethylenes and which must therefore have the structure XVIII. This compound is converted almost quantitatively into the 1,4-diphenyl-4-methoxy-3-butene-1,2-dione XXIV when refluxed with methanol, and into the ethyl analog with ethanol, reactions which appear to confirm the structure XVIII. These relations may be represented as follows



$$\left.\begin{array}{l} C_6H_5COC(OCH_3){=}CHCOC_6H_5 \\ C_6H_5COC(OH){=}CHCOC_6H_5 \end{array}\right\} \xrightarrow{SOCl_2} \left[C_6H_5CO\underset{\substack{|\\Cl}}{C}\begin{pmatrix} OCH_3 \\ \text{or} \\ OH \end{pmatrix} CH{=}\underset{\substack{|\\OSOCl}}{C}C_6H_5\right] \longrightarrow$$

$$\underset{\text{XVIII}}{C_6H_5COCOCH{=}\underset{\substack{|\\Cl}}{C}C_6H_5} \xrightarrow[CH_3OH]{\text{Reflux}} \underset{\text{XXIV}}{C_6H_5COCOCH{=}\underset{\substack{|\\OCH_3}}{C}C_6H_5}$$

These studies are being continued.

Experimental Part

The various reactions described in the foregoing account were all carried out according to the following procedure.

A 1-g. sample of the compound being tested was mixed in a test-tube with 2 g. of phosphorus pentahalide. Those reactions given as proceeding at 25–40° melted down spontaneously with the evolution of hydrogen chloride and with a slight rise in temperature to not over 40°. Those indicated as proceeding at 100° did not react spontaneously, but did so upon heating in a water-bath; these were heated for a short time (five to fifteen minutes) with stirring to complete the reaction. The mixtures were worked up by decomposing in ice and crystallizing the precipitated organic material from a suitable solvent, usually ethanol. The products were identified in every case by mixed melting points with known materials. The yields are given in the table.

	Action of PCl_5		Action[a] of PBr_5,	Action[b] of $SOCl_2$,
Substance	Temp., °C.	% yield of II	% yield of VII	product, % yield
I	100	90	85	[c]
III	100	95	..	..
V	100	70	75	..
V	25–40	80[d]	..	..
VI	100	50	..	[c]
IV	100	80	..	[c]
XII	100	35	..	II, 90
XI	25–40	75	..	II
IX	100	[e]	80	[f]
X	100	50	..	[c]
XXV[g]	100	[c]	..	[c]
XXVI[g]	25–40	10[h]	..	X
XXVII[g]	25–40	75[h]	..	..
XVII[i]	25–40	95	..	[c]
XVII[j]	25–40	90	60	[c]
XVIII	25–40	90	..	[c]
XIII[k]	100	90	50	X, 90
XIII[l]	25–40	90[m]	..	..
XIII[k]	25–40	90[m]	..	[f]
XIV[l]	25–40	90	..	II, 90
XIV[k]	100	65	..	[c]
XVI	25–40	80	95	XVIII, 90
XV	25–40	80	..	XVIII, 50

[a] Reactions carried out at 100°, and [b] at refluxing temperature. [c] No reaction occurred and the starting material was recovered unchanged. [d] The product was diphenylacetoxychlorofuran, VI. [e] The product was a new substance which has not yet been identified. [f] The product was resinous. [g] XXV = *dl* and *meso* dibenzoyldichloroethanes; XXVI = dibenzoylhydroxyethane; XXVII = dibenzoylmethoxyethane. [h] The product was dibenzoylchloroethane, X. [i] Methyl ether. [j] Ethyl ether. [k] *Trans*. [l] *Cis*. [m] The product was diphenylchlorofuran, III.

The action of phosphorus pentachloride and phosphorus oxychloride (with a little added phosphorus trichloride, and with hydrogen chloride bubbling through the mixture) at 100° on *dl* and *meso* dibenzoyldichloroethanes in both cases gave largely unchanged material and traces only of diphenyldichlorofuran.

The Action of Phosphorus Pentachloride on Diphenyldichlorofuran.—In some experiments, notably those with the 1,4-diphenyl-4-alkoxy-3-butene-1,2-diones, the action of phosphorus pentachloride at 100° produced *cis* dibenzoyldichloroethylene. The expected diphenyldichlorofuran, which is undoubtedly first formed, is itself acted upon under slightly more drastic conditions than those ordinarily involved in the various reactions listed in the above table. The best conditions for bringing about this opening of the furan ring are illustrated in the following experiment. A mixture of 1 g. of diphenyldichlorofuran, 10 g. of phosphorus pentachloride, and 20 cc. of phosphorus oxychloride was refluxed gently for fifteen minutes and decomposed in water. The product was crystallized from ethanol and identified by mixed m. p. as dibenzoyldichloroethylene; yield 80–90%. Under approximately equivalent conditions the *trans* isomer is stable.

The action of phosphorus oxychloride on *trans* dibenzoylethylene, with subsequent hydrolysis of the resulting mixture in water, gave a 90% yield of dibenzoylchloroethane.

The reactions with thionyl chloride were carried out with a ratio of reagent to substance of 15 cc. to 1 g., at refluxing temperature (unless otherwise specified); the time of heating was usually one hour. The product was isolated by evaporation of the excess of reagent under reduced pressure and recrystallization of the residue from ethanol. The results are included in the table.

1,4-Diphenyl-4-chloro-3-butene-1,2-dione, XVIII.—A 0.5-g. sample of dibenzoylmethoxyethylene (or of dibenzoylethenol) 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).