room temperature; crude yield, 95%. After washing with ether, the product was crystallized from 60% acetone; colorless crystals, m. p. 107–108°, soluble in alcohol.

Anal. Calcd. for $C_{25}H_{33}O_9N$: C, 63.74; H, 6.31. Found: C, 64.08; H, 6.50.

α-Carbethoxy-β-phenylmaleinanil (VI).—A sample of V (3 g.) was subjected to vacuum distillation; a water-white distillate was obtained, distilling at 101–102° at 25 mm. Fractional distillation of this liquid showed it to consist largely of diethyl malonate, verified by conversion to malonamide. A low-boiling fraction was evidently ethyl alcohol. The residue from the vacuum distillation was dissolved in 20 cc. of diethyl ether, and diluted with 100 cc. of petroleum ether. Hard yellow crystals separated after two hours of cooling; it recrystallized from 80% alcohol as yellow rhombic crystals, m. p. 111°, soluble in alcohol, ether, benzene; yield, 75%.

Anal. Calcd. for $C_{19}H_{15}O_4N$: C, 71.03; H, 4.67; N, 4.36. Found: C, 71.09; H, 4.79; N, 4.31, 4.56.

α-Carbethoxy-β-phenylsuccinanil (VII).—One gram of VI was dissolved in 15 cc. of boiling alcohol and to this was added 1 g. of sodium hyposulfite in 5 cc. of hot water. The mixture was heated for five minutes until it became colorless. Upon addition of 75 cc. of water and cooling, a white oil separated, which gradually solidified to white needles from 10% alcohol, m. p. 104–105°, soluble in alcohol, ether, acetone, ethyl acetate, chloroform, benzene; yield, 85%.

Anal. Calcd. for $C_{19}H_{17}O_4N$: C, 70.59; H, 5.26; N, 4.33. Found: C, 70.60; H, 5.28; N, 4.26.

Phenylsuccinanil from VII.—A solution of 1 g. of VII in 15 cc. of alcohol and 15 cc. of concd. hydrochloric acid was refluxed for one hour and then evaporated to dryness on a steam-bath. The residue was extracted with three 10-cc. portions of boiling water. Concentration of the extract to one-third its volume and cooling gave white needles, m. p. 137–138°; yield, 40%. There was no lowering of melting point when mixed with a known sample.

Summary

Benzoylformanilide condenses in the presence of diethylamine with one mole of acetone and two moles of diethyl malonate to give products analogous to those of isatin. The diethyl malonate product is decomposed by heat, losing a molecule of diethyl malonate and forming a maleinanil derivative through ring closure.

Ethyl phenylacetate reacts slowly with benzoylformanilide under similar conditions to yield symmetrical diphenylmaleinanil.

NEW YORK, N. Y. RECEIVED AUGUST 31, 1935

[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORIES OF THE R. & H. CHEMICALS DEPARTMENT OF E. I. DU PONT DE NEMOURS & CO., INC.]

The Preparation of High Molecular Weight Acyloins

BY V. L. HANSLEY

The simultaneous reaction and condensation of aliphatic esters by means of sodium to give α,β-keto alcohols, the so-called acyloins, has been limited in previous investigations to esters of acids of six or less carbon atoms. Previous work along this line has been summarized by Corson and his co-workers.[1]

By the use of different solvents and by making radical changes in reaction conditions, we have been able to extend this series of acyloins from 12 to 36 carbon atoms and to shorten the reaction time considerably.

The reaction between sodium and the esters takes place essentially quantitatively according to the following equation, and neither reactant need be employed in excess.

(a) $$2RCOOCH_3 + 4Na \longrightarrow \begin{matrix} RCONa \\ \| \\ RCONa \end{matrix} + 2CH_3ONa$$

(b) $$\begin{matrix} RCONa \\ \| \\ RCONa \end{matrix} \xrightarrow{HOH} \begin{matrix} RCOH \\ \| \\ RCOH \end{matrix} \xrightarrow{\text{Rearrangement}} \begin{matrix} RCHOH \\ \| \\ RC{=}O \end{matrix}$$

While previously recommended methods for the preparation of butyroin and other low molecular weight acyloins[2] do not suggest any difficulty in the preparation of the higher molecular weight acyloins, the work of Corson and his co-workers[1] indicates that the described methods of preparation fail when applied to these higher esters.

The failure of these investigators to obtain acyloins from acids of greater than six carbon atoms was apparently due to the insolubility of the reaction products at the temperatures employed in the particular reaction media used. Previous investigators carried out their reactions in ether or benzene at room temperature or lower, allowing even days for the reaction to take place. A few previous attempts were also made to carry

(1) Corson, Benson and Goodwin, THIS JOURNAL, **52**, 3988 (1930); *cf* Snell and McElvain, *ibid.*, **53**, 750 (1931).

(2) Snell and McElvain, "Organic Syntheses," J. Wiley & Sons, Inc., 440 Fourth Ave., New York City, 1933, Vol. XIII, pp. 24–26.

out the preparation of acyloins in boiling toluene[1] but the reaction products could not be worked up.

By going to reaction conditions where the sodium was kept in a molten and finely dispersed state and the reaction products kept "in solution," we have been able to obtain 80–95% yields of acyloins from aliphatic esters of 8 to 18 carbon atoms. Practically quantitative reaction was obtained between ester and sodium without employing either reactant in excess. Besides carrying out the reaction above the melting point of sodium, the rate and mode of addition of ester, molecular weight of ester and concentration and solubility of reaction products all influenced the fluidity of the reaction mixture and hence the yield. Xylene and toluene were equally good solvent media, provided impurities were absent which would react with sodium. Likewise, the esters had to be free of organic acid or hydroxyl compounds. Both of these tended to cause the reaction mixture to gel, after which the useful reaction between sodium and ester practically ceased. In such cases a large part of the sodium remained unreacted.

The amount of acyloin that could be prepared in a given amount of solvent was greater with methyl laurate than any other ester tried. Esters of higher molecular weights formed more insoluble sodium derivatives while lower molecular weight esters inherently gave a greater amount of sodium methylate which could only be held in "pseudo solution" by use of more solvent. This is probably one of the reasons why previous investigators failed to obtain satisfactory reaction in toluene. They were using acid esters of too low a molecular weight in too high concentration when employing toluene as the solvent. For similar reasons they encountered difficulty when attempting the reaction of high molecular weight esters with sodium in ether at room temperature. In the preparation of lower molecular weight acyloins, *e. g.*, from caproic or caprylic acids, the use of the *n*-butyl or secondary butyl ester permitted the preparation of a considerably larger quantity of acyloin per unit volume of solvent than was possible when the methyl esters were employed.

The reaction products obtained from the straight chain aliphatic acid esters were characterized as the corresponding α,β-keto alcohols by the analysis of their acetates and osazones. The melting points of all the acyloins prepared fall on a smooth curve which flattens out considerably at about 80° when the length of the carbon chain reaches 32–36 carbon atoms. The acyloins are all waxy, white, easily crystallizable compounds, the solubilities of which vary widely from capryloin to stearoin. The stability of the acyloins was found to increase with the molecular weight. A tendency to polymerize was noted in the case of butyroin and to some extent with capronoin. Little, if any, polymerization resulted during the isolation of acyloins from acids of eight or more carbon atoms.

Experimental Part

Preparation of the Methyl Esters.—The mixture of methyl esters obtained by the esterification of commercial coconut oil fatty acids in the usual manner was subjected to careful vacuum fractionation at 15 mm. in 5-liter batches. Pure cuts of 0.2–0.3° range were made taking the boiling points of Haller and Youssoufian[3] for the esters of even carbon atom acids from caproic to myristic esters. Methyl butyrate was obtained from the Eastman Kodak Co., their better grade being usable without further purification. Stearate and palmitate esters were obtained from a catalytically hydrogenated palm oil which was converted to the methyl esters. Methyl palmitate and stearate were fractionated from this ester mixture at 15 mm. The boiling points noted, 190.5° for the palmitate and 212.3° for the stearate, are somewhat lower than those recorded in the literature, 195–196 and 215°, respectively.[3] The nonylic acid was obtained by the ozonolysis of oleic acid and esterified in the usual manner.

Preparation of the Acyloins.—One hundred and fifteen grams of sodium (5 atoms) together with 3 liters of C. P. xylene were charged into a 5-liter 3-necked flask immersed in an oil-bath at 105°. The flask was fitted with a rather high-speed stirrer (2000–2500 r. p. m.). The air over the xylene was replaced by nitrogen or other inert gas. When the temperature of the xylene reached 105° and the sodium melted, the stirrer was started and the sodium dispersed in a finely divided state in the xylene. Methyl laurate, 535 g. or the equivalent quantity of another ester (2.5 moles) was then started into the reaction flask from a separatory funnel. The addition was at such a rate that the temperature due to heat of reaction did not rise above 110°. This required about one hour. Stirring was continued for one-half hour after the ester had been added.

Small particles of unchanged sodium were then decomposed by the addition of an excess of methanol (one to two moles). Then, after cooling to about 80° water, 0.5 to 1.0 liter, was cautiously added until the alkali was taken into an aqueous layer which was then removed by decantation. After one or two more washings with water, the remaining alkali was neutralized with a slight excess of mineral acid and the excess acid finally neutralized with sodium bicarbonate.

The xylene was removed by steam distillation from the acyloin and the resulting oily layer poured into a suitable vessel to solidify. The impure product contained 80–90% acyloin. The acyloins from methyl caproate, laurate and

(3) Haller and Youssoufian, *Compt. rend.*, **143**, 805 (1905).

myristate were purified by crystallization from 95% alcohol but acyloins corresponding to methyl palmitate and stearate were found to crystallize better from trichloroethylene or acetone.

Other acyloins prepared by this procedure are given in Table I.

TABLE I

SATURATED ALIPHATIC ACYLOINS PREPARED

Acyloin name	Observed m. p., °C.	M. p. of osazone, °C.
Acetoin	Not prepared	242[4]
Butyroin	−10	140–141[1]
Capronoin[1]	+ 9	119–120
Capryloin	39	Not prepared
Nonyloin	45	Not prepared
Caprinoin	51–52	79–80
Lauroin	61–62	61–63
Myristoin	71–72	44–46
Palmitoin	77–78	Not prepared
Stearoin	82–83	Not prepared

ANALYSES OF COMPOUNDS

Compound	Formula		Calcd.	Found
Capronoin osazone	$C_{24}H_{34}N_4$	N	14.8	13.8
Caprinoin osazone	$C_{32}H_{50}N_4$	N	11.4	10.9
Lauroin osazone	$C_{36}H_{58}N_4$	N	10.2	9.6
Myristoin osazone	$C_{40}H_{66}N_4$	N	9.3	8.7
Caprinoin acetate	$C_{22}H_{42}O_3$	CH_3CO	12.1	11.9
Lauroin acetate	$C_{26}H_{50}O_3$	CH_3CO	10.5	10.9
Myristoin acetate	$C_{30}H_{58}O_3$	CH_3CO	9.24	9.28
Palmitoin acetate	$C_{34}H_{66}O_3$	CH_3CO	8.23	7.98

Hydrogenation of the Acyloins to Substituted Ethylene Glycols.—All of the acyloins upon catalytic hydrogenation with a platinum catalyst at room temperature or nickel at 125–150° were converted into the corresponding symmetrically substituted dialkyl ethylene glycols. Due to the double asymmetry in the glycol molecule two forms should occur, meso and racemic. While α- and β- (low and high melting) forms of the glycols from butyroin and capronoin have been described[5] and a liquid isomeric mixture of glycols described as a by-product in the sodium reduction of methyl caprylate,[6] there is still some doubt as to whether the low melting glycols were actually obtained. We were able to obtain only the high melting form pure in each case. The four glycols prepared are shown in Table II together with the previously described glycols from butyrate and caproate esters.

TABLE II

SYMMETRICALLY SUBSTITUTED ETHYLENE GLYCOLS

Ethylene glycol RCHOHCHOHR, R =	Parent ester	M. p., °C.
$C_{17}H_{35}$	Stearate	123–124
$C_{13}H_{27}$	Myristate	124
$C_{11}H_{23}$	Laurate	125–126
C_7H_{15}	Caprylate	129–130
C_5H_{11}[5]	Caproate	135–136
C_3H_7[5]	Butyrate	123–124

ANALYSES

Ethylene glycol diacetate	Formula	Acetyl values Calcd.	Found
sym-Diheptyl-	$C_{20}H_{38}O_4$	327	320
sym-Diundecyl-	$C_{28}H_{54}O_4$	248	245
sym-Tridecyl-	$C_{32}H_{62}O_4$	220	215
sym-Diheptadecyl-	$C_{40}H_{78}O_4$	180	175

Oxidation of Acyloins to the Diketones.—A 1.0202-g. quantity of lauroin was treated in dry chloroform solution with a 100% excess of Wijs solution[7] and allowed to stand overnight: 0.716 g. of iodine was consumed; calcd. for the oxidation of this amount of lauroin to the diketone, 0.695 g. of iodine. The diketone crystallized well from methanol, giving the characteristic yellow diketone which melted sharply at 71–71.5°.

The properties and further reactions of these condensation products will be taken up in a subsequent paper.

Summary

The preparation of the α,β-keto alcohols or acyloins has been carried up to and including stearoin. All acyloins from esters of acids above caproic are new. By the catalytic hydrogenation of these keto alcohols the symmetrically substituted dialkyl ethylene glycol series has been extended from 12 to 36 carbon atoms in the molecule.

The acetates and osazones of the acyloins and the diacetates of the corresponding glycols were also prepared.

One of the acyloins, lauroin, was oxidized to the corresponding *sym*-α,β-diketone.

NIAGARA FALLS, NEW YORK RECEIVED JULY 26, 1935

(4) L. A. Higley, *Am. Chem. J.*, **37**, 316 (1907).

(5) Bouveault and Blanc, *Compt. rend.*, **136**, 1677 (1903); *Bull. soc. chim.*, [3] **31**, 670 (1904).

(6) Bouveault and Locquin, *ibid.*, [3] **35**, 629–43 (1906).

(7) Lewkowitsch, "Oils, Fats and Waxes," The Macmillan Co. New York City, 1921, Vol. I, p. 416.