

Anal. Calcd. for $C_{12}H_{12}N_2O_5$: C, 54.54; H, 4.58; N, 10.6. Found: C, 54.72, 54.40; H, 4.46, 4.59; N, 10.5, 10.8.

For comparison *N-p-nitrobenzylsuccinimide* (II) was prepared according to a known procedure.¹⁰ Its m.p. was 152–154° (lit. 150–152°)¹⁰; λ_{max} in absolute ethanol 266 $m\mu$; $\log \epsilon$, 4.01. The m.p. of a mixture of I and II was 120–125°.

Hydrolysis of DL-N- α -methoxy-p-nitrobenzylsuccinimide. (a) A 1.0-g. sample of I was heated briefly with 20 ml. of saturated aqueous barium hydroxide. The dark alkaline solution was extracted with ether after cooling, the extract dried with sodium sulfate and evaporated to give 0.2 g. (69%) of *p-nitrobenzyl alcohol*, m.p. 92–93° (lit. 93°)¹¹ which was converted to *p-nitrobenzyl acetate*, m.p. 76–78° (lit. 78°).¹² The basic mother liquor was acidified with hydrochloric acid and yielded 0.2 g. (63%) of *p-nitrobenzoic acid*, m.p. 239–240° (lit. 242.4°)¹¹ after recrystallization from water.

(b) An 0.7-g. sample of I was distilled slowly with 25 ml. of 5% hydrochloric acid. *p-Nitrobenzaldehyde* distilled with the steam and the water was replaced in the reaction mixture from time to time. After about 3 hr. a clear solution was obtained. Heating was continued for another hour, then both reaction mixture and distillate were cooled to 5°. The main crop of aldehyde was isolated from the distillate

(10) S. Hoogewerff and W. A. Van Dorp, *Rec. trav. chim.*, **18**, 358 (1899).

(11) *Handbook of Chemistry and Physics*, 34th edition, The Chemical Rubber Publishing Co., Cleveland, Ohio, 1952.

and combined with a small amount filtered from the acidic reaction mixture. The total yield was 0.3 g. (75%), m.p. 105–106° (lit. 106.5°).¹¹ The acidic solution was then evaporated and the residue was recrystallized from water. A crop of 130 mg. (41%) of succinic acid, m.p. 189–190° [lit. 185° (189–190°)]¹¹ was obtained. When the mother liquor of the succinic acid was made alkaline, the presence of ammonia was detected by its odor and further established with Nessler's reagent. All solid products isolated in the course of these experiments were identified by mixed melting point determinations with authentic samples.

Reaction of p-nitrobenzaldehyde dimethyl acetal with NBS. A mixture of 3.5 g. of *p-nitrobenzaldehyde dimethyl acetal*,¹³ 3.5 g. of NBS, and 70 ml. of carbon tetrachloride was refluxed. After about 4 hr. all the NBS had reacted and the mixture was filtered. Most of the product crystallized on cooling but an additional amount was obtained on evaporation of the mother liquor. The two crops were combined and recrystallized from dilute methanol and benzene-petroleum ether respectively to give 3.0 g. (91%) of methyl *p-nitrobenzoate*, m.p. 94–95° (lit. 96°).¹¹ No depression of this melting point was observed on admixture to an authentic sample.

AMHERST, MASS.

(12) The staff of Hopkins and William Research Laboratory, *Organic Reagents for Organic Analysis*, Chemical Publishing Co., Inc., Brooklyn, N. Y., 1950.

(13) E. Fischer and G. Giebe, *Ber.*, **30**, 3057 (1897)

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

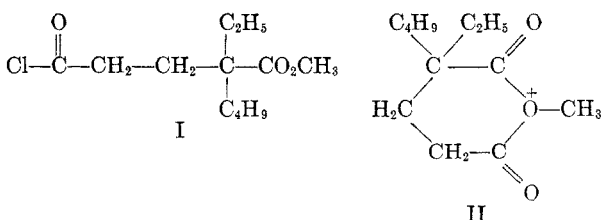
Structure of Succinyl Dichloride and of Certain Other Potentially Cyclic Difunctional Compounds¹

JAMES CASON AND ELMER J. REIST

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Examination of the infrared absorption by carbonyl in succinyl dichloride furnishes additional evidence that this compound exists in the open chain form. Products of the known reactions of this dichloride may be satisfactorily correlated on the basis of the open chain structure, provided recognition be taken of the fact that γ -keto acid chlorides exist entirely (or almost so) in the cyclic form. δ -Ketoanantyl chloride is also in the cyclic form. Certain derivatives of α -butyl- α -ethylglutaric acid, other than the ester acid chlorides, are found to exist partly or largely in the cyclic form.

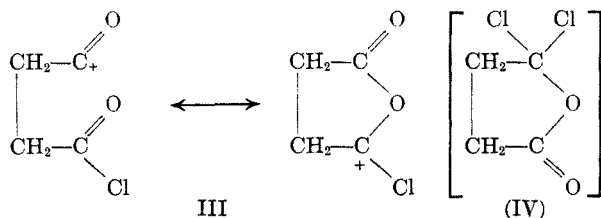
In a previous investigation in this laboratory,² data were assembled which demonstrated that the ester acid chlorides (I, or its isomer) of α -butyl- α -ethylglutaric acid exist entirely as open chain structures at room temperatures, and rearrange rather



(1) This investigation was supported in part by a research grant (E-86) from the National Institutes of Health, U. S. Public Health Service. A part of these data was presented at the 127th meeting of the American Chemical Society, Cincinnati, Ohio, March 30, 1955.

(2) J. Cason and R. D. Smith, *J. Org. Chem.*, **18**, 1201 (1953).

slowly by way of a cyclic structure at temperatures in the range 120–150°. Rearranged products were obtained only in those reactions where a Lewis acid extracts halogen to yield as a reaction intermediate the cyclic oxonium ion, shown in one resonance form in II. In view of the stability of the ester acid chlorides such as I, it was suggested² that succinyl dichloride also exists as an open chain compound and that cyclic reaction products are formed from the open chain structure by way of cyclic intermediates such as are shown in two resonance forms in III.



Numerous physical measurements have indicated that succinyl dichloride exists predominantly in the open chain form and that the cyclic form (IV) is a minor component, if present at all. These measurements have included molecular volume,^{3,4} refractivity,⁵ parachor,⁶ and dipole moment.⁷ Nevertheless, formation of cyclic products has been widely attributed⁸ to equilibration of the open chain form with a small amount of the cyclic form. Ratio of products would depend on relative concentration of the two forms, as well as their reactivities; however, formation of large ratios of cyclic products from a small ratio of IV in the dichloride would require a facile equilibration at room temperature between the two forms of the dichloride. This is contraindicated by the stability of the ester acid chloride.

In the present work, additional support for the open chain form of succinyl dichloride has been secured by examination of the infrared spectrum. In case any cyclic form were present in succinyl dichloride, it would be expected to absorb in the infrared at a different wave length than a normal acid chloride, and other investigations to be described below support this expectation; however, the only carbonyl absorption observed is at 5.60μ , the normal location of absorption in low molecular weight acid chlorides. Further, quantitative determination of absorption should reveal⁹ presence of the cyclic form, for formula IV contains only one carbonyl, whereas the open chain form contains two carbonyl groups. As shown in Fig. 1, the absorption of succinyl dichloride calculated on the basis of two carbonyl groups per mole is quite consistent with that of the monofunctional caprylyl chloride, as well as that of pimelyl dichloride whose functional groups are too remote to allow formation of a cyclic form of a favored ring size.

It proves possible to correlate much of the data in the literature if it be assumed that formation of cyclic products from succinyl dichloride occurs only in reactions wherein extraction of halogen by a Lewis acid generates a cyclic reaction intermediate (III). In contrast with the case of the ester acid chlorides,² however, these correlations do not constitute evidence for a single reaction path. As will

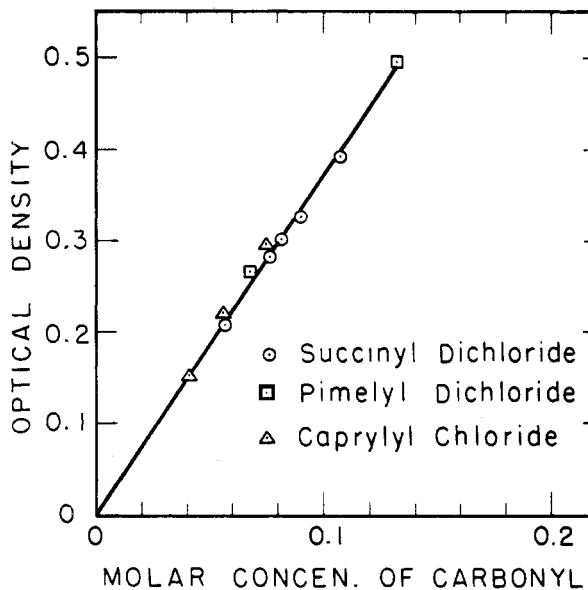


Fig. 1. Infrared absorption of acid chlorides in carbon tetrachloride solution

be developed in discussion to follow, an alternate route to cyclic products from succinyl dichloride results from cyclization of certain of the products formed after reaction of only one acid chloride grouping. In some instances, this second pathway seems clearly indicated.

Reaction of succinyl dichloride with diethylzinc has been reported¹⁰ to yield γ -ethyl- γ -caprolactone, consistent with previous proposals¹¹ concerning the mechanism of reaction of cadmium and zinc reagents. The Friedel-Crafts reaction of succinyl dichloride with benzene has been reported¹² to give a mixture of open chain and cyclic products, while either catalytic¹³ or chemical¹⁴ reduction yields butyrolactone. In contrast, reaction of succinyl dichloride with alcohols¹⁵ yields only normal esters, and the pyrrole Grignard reagent has been reported¹⁶ to yield the open chain product. The latter observation is consistent with the different reaction mechanisms of magnesium and zinc reagents. Reaction with amino esters¹⁷ or aniline³ also yielded open chain products, as would be expected. Cyclic products have been claimed⁸ for reactions with ammonia and methylamine; however, purification of the products was difficult and identification leaves much to be desired; the reaction product with

(3) G. F. Morrell, *J. Chem. Soc.*, **105**, 1733 (1914).

(4) E. Ott, *Ann.*, **392**, 245 (1912).

(5) K. v. Auwers and M. Schmidt, *Ber.*, **46**, 457 (1913).

(6) F. B. Garner and S. Sugden, *J. Chem. Soc.*, **2877** (1927).

(7) G. T. O. Martin and J. R. Partington, *J. Chem. Soc.*, **1178** (1936).

(8) B. H. Chase and D. H. Hey, *J. Chem. Soc.*, **553** (1952), also references to earlier work cited therein.

(9) The significance of the quantitative absorption by carbonyl is decreased by the fact that carbonyl in the cyclic compound may absorb more strongly than that in the open chain compound; in fact, such is probably the case. In the instance of the γ -keto acid chloride, described below, where the cyclic compound is definitely in hand, ϵ_{\max} for carbonyl in the cyclic acid chloride is about 590, as opposed to about 370 for an open-chain acid chloride.

(10) G. Wischin, *Ann.*, **143**, 259 (1867); A. Emmert and R. Friedrick, *Ber.*, **15**, 1851 (1882).

(11) J. Cason, *J. Org. Chem.*, **13**, 227 (1948).

(12) V. Auger, *Bull. soc. chim. France*, [2], **49**, 345 (1888); V. Auger, *Ann. chim. phys.*, [6], **22**, 313 (1891).

(13) N. Fröschl, A. Maier, and A. Heuberger, *Monatsh.*, **59**, 256 (1932); N. Fröschl, A. Maier, and A. Heuberger, *J. prakt. Chem.*, **144**, 217 (1936).

(14) A. Saytzeff, *Ann.*, **171**, 258 (1874).

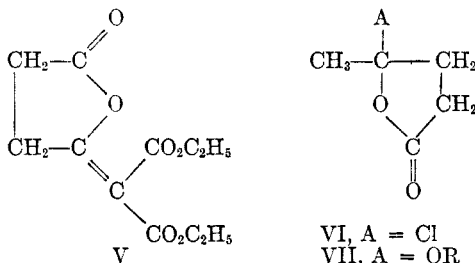
(15) R. Meyer and K. Marx, *Ber.*, **41**, 2459 (1908).

(16) W. Tschelinzeff and D. Skworzoff, *J. Russ. Phys. Chem. Soc.*, **47**, 170 (1915); *Chem. Zentr.*, **1916**, **1**, 789.

(17) T. Curtius and W. Hechtenberg, *J. prakt. Chem.*, **105**, 313 (1923).

ammonia exhibited properties suggestive of succinimide.

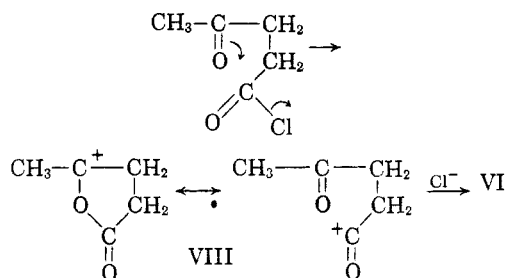
Although acylation of malonic ester by an acid chloride no doubt involves displacement of halogen by the enolate ion, the reaction product of malonate and succinyl dichloride has been proved¹⁸ beyond any reasonable doubt to have structure V.



Although this structure appears to have arisen from a cyclic formula for succinyl dichloride, its origin from the open chain form of succinyl dichloride may be formulated if there be considered the fact that γ -keto acid chlorides *do exist* in the cyclic form at room temperature. The most carefully investigated γ -keto acid chloride is levulinyl chloride, first prepared by L. Wolff¹⁹ by the reaction of hydrogen chloride with α -angelica lactone. Although Wolff assumed levulinyl chloride to be γ -chloro- γ -valerolactone (VI), from his method of preparation, von Auwers and Schmidt⁵ concluded from a study of molecular refractivities that it has the open chain structure. Helberger²⁰ regarded levulinyl chloride as probably having the cyclic structure (VI) assigned by Wolff, and rationalized his obtaining of an open-chain product in the Friedel-Crafts reaction as rearrangement caused by aluminum chloride. More recently, Langlois and H. Wolff²¹ have offered excellent chemical evidence that the cyclic formula is correct, by isolation of the pseudo esters (VII) of levulinic acid by reaction of the acid chloride with alcohols. Since the pseudo esters were rearranged to normal open chain esters in presence of hydrogen chloride, the cyclic structure for the acid chloride is strongly indicated.

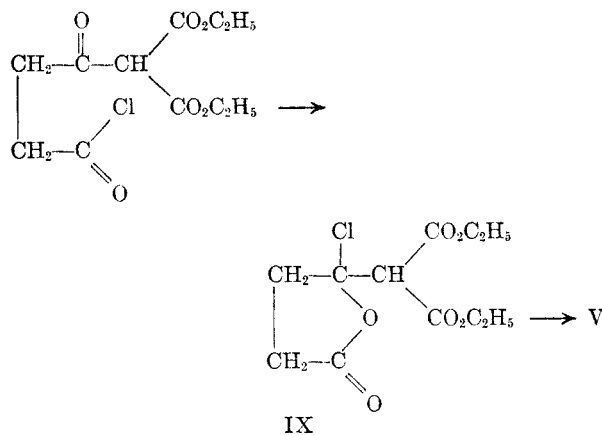
In the present investigation, it has been found that the infrared spectra of levulinyl chloride and also of γ -ketocaproyl chloride offer additional evidence that these γ -keto acid chlorides exist at room temperature entirely, or predominantly, as cyclic structures. In each, there is only one absorption band²² in the carbonyl region, at 5.54μ , a wavelength characteristic of neither a lower molecular weight open-chain acid chloride (5.57 – 5.60μ) nor a ketone (5.80 – 5.86μ). Thus, although a diacid di-

chloride and an ester acid chloride are stable in the open chain form, presence of alkyl on the second carbonyl group causes ready conversion to the cyclic structure. It has previously been observed²³ that a γ -alkoxy acid chloride is converted to the γ -chloro ester on heating to 100° in absence of any catalyst; so ether oxygen appears able to displace halogen from the acid chloride, without assistance from a Lewis acid. Similarly, the carbonyl oxygen in a ketone seems able to displace halogen even at room temperature to give the cyclic ion, VIII, which may react to give the cyclic structure, VI. The superior efficacy of keto oxygen in displacing



halogen would argue for the greater basicity of this oxygen than the oxygen in an ester or acid chloride.

In view of the existence of γ -keto acid chlorides in a cyclic form, the conversion of malonic ester to structure V by reaction with succinyl dichloride would be expected to proceed by normal acylation of malonic ester to give the γ -keto acid chloride which would cyclize to IX, a structure which would readily lose hydrogen chloride.



Since δ -lactones form less readily than do γ -lactones, it was deemed of interest to examine the infrared spectrum of δ -ketoenanthyl chloride. This substance exhibited a strong carbonyl band²⁴ at 5.65μ , however; there was always a weaker band at 5.94μ , and there was no significant absorption in

(18) P. Ruggli and A. Maeder, *Helv. Chim. Acta*, **26**, 1476 (1943).

(19) L. Wolff, *Ann.*, **229**, 249 (1885).

(20) J. H. Helberger, *Ann.*, **522**, 269 (1936).

(21) D. P. Langlois and H. Wolff, *J. Am. Chem. Soc.*, **70**, 2624 (1948).

(22) In a measurement on a thin film giving an optical density of 1.3 for the 5.54μ band, a questionable band at 5.83μ had an optical density of about 0.01.

(23) V. Prelog and S. Heimbach-Juhász, *Ber.*, **74**, 1702 (1941).

(24) This wave length, about 0.1μ above the position of absorption for the acid chlorides with five atoms in the ring, is the expected position for the cyclic acid chloride with six atoms in the ring. As noted in Table I, a band also occurs at this position for γ -ethyl- γ -formylcaprylyl chloride.

the 5.80μ region. Since analysis for chlorine in this acid chloride gave a value considerably below theory, the absorption at 5.94μ must arise from presence in the acid chloride of enol lactone resulting from loss of hydrogen chloride from the cyclic acid chloride. It may be recalled that in the case of a five-atom ring, as in α -angelica lactone, hydrogen chloride adds to the unsaturated lactone.¹⁹

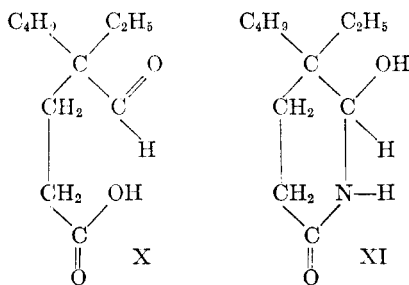
Examination of the infrared spectra of several derivatives of γ -ethyl- γ -formylcaprylic acid (X) indicates interesting variations between open chain and cyclic structures. The absorption bands of interest in this connection are listed in Table I.

TABLE I

INFRARED ABSORPTION OF CERTAIN DERIVATIVES OF
 γ -ETHYL- γ -FORMYL-CAPRYLIC ACID

Compound	Absorption Bands Related to Carbonyl Structure, μ
γ -Ethyl- γ -formylcaprylic acid (X)	3.68, 5.83, 5.88
γ -Ethyl- γ -formylcaprylyl chloride	3.70, 5.59, 5.67, 5.83
Ethyl γ -ethyl- γ -formylcaprylate	3.70, 5.79
γ -Ethyl- γ -formylcaprylamide (XI)	2.85, 6.01

It is indicated that γ -ethyl- γ -formylcaprylic acid is largely in an open-chain structure since its spectrum exhibits a band corresponding to the normal position for hydrogen on carbonyl (3.68μ), as well as the carbonyl and carboxyl bands. The ester of this acid, although prepared from the acid chloride, also appears to be largely open chain (aldehyde and ester bands not resolved), whereas the amide (XI) appears to be largely a cyclic structure. Since the same compound was obtained by partial hydrolysis of γ -ethyl- γ -formylcaprylonitrile or by reaction of ammonia with γ -ethyl- γ -formylcaprylyl chloride, and since there is infrared absorption in the hy-



droxyl region as well as near that of an open chain amide, formulation as in XI seems indicated, rather than as the isomer with oxygen in the ring. The cyclic nature of this amide is also indicated by its decomposition on melting and by its melting point of 159 – 160° , remarkably high for an aliphatic amide.

γ -Ethyl- γ -formylcaprylyl chloride is especially interesting in that it exists partly in the open chain

form and partly in the cyclic form. The bands at 5.59μ and 5.83μ , from the acid chloride and aldehyde groups, are of nearly equal intensity, and the optical density of the 5.67μ band from the cyclic form is about 40% greater than that of the other two. In this compound, it should be noted that formation of an enol lactone with endocyclic double bond is impossible without rearrangement, on account of absence of hydrogens on the atom adjacent to the carbon involved in lactone formation in the cyclic form.

Chemical reactions of certain of the compounds discussed in this paper, yielding products consistent with the proposed structures, will be described in future reports from this laboratory.

EXPERIMENTAL²⁵

Succinyl dichloride was not obtained when succinic acid was treated with thionyl chloride alone; the product was succinic anhydride. The dichloride was also not obtained when thionyl chloride was used in the presence of one molar equivalent of pyridine; the product was tar. The acid chloride could be obtained by the use of thionyl chloride in presence of a catalytic amount of pyridine or (in poorer yield) by use of phosphorus pentachloride. The infrared spectra of samples prepared by the two methods were qualitatively and quantitatively identical; the carbonyl peak was at 5.60μ .

A. A mixture of 20 g. (0.17 mole) of succinic acid, 67 ml. (0.84 mole) of purified thionyl chloride, and 4 drops of dry pyridine was heated under reflux for 3 hr. After excess thionyl chloride had been removed at reduced pressure, the residue was distilled to yield 21 g. (81%) of succinyl dichloride, b.p. $65^\circ/5$ mm. Similar results were obtained when succinic anhydride was substituted for succinic acid.

B. According to a published procedure,¹² a mixture of 20 g. (0.17 mole) of succinic acid and 80 g. (0.38 mole) of phosphorus pentachloride was heated under reflux for 48 hr. in an oil bath heated to 120° . At the end of the heating period, the dark mixture was treated with 2 ml. of glacial acetic acid to decompose excess phosphorus pentachloride, the mixture was filtered through glass wool, and phosphorus oxychloride was removed under reduced pressure. Distillation of the residue in a Claisen flask yielded 17.8 g. of yellow acid chloride, which was redistilled in the column to yield 14 g. (53%) of colorless product, b.p. $69^\circ/5$ mm.

Pimelyl dichloride was prepared in 81% yield from recrystallized pimelic acid (m.p. 104.0 – 104.7°) by procedure (A) described for succinyl dichloride, except that pyridine was omitted. Spectra were determined on the center cut of a redistilled sample, b.p. $113^\circ/5$ mm.; the carbonyl peak was at 5.58μ .

Caprylyl chloride was prepared from fractionally distilled caprylic acid by the procedure used for pimelyl dichloride.

(25) Melting points are corrected and boiling points are uncorrected. Distillations, except where otherwise specified, were through a half-meter column of the simple Podbielniak type (J. Cason and H. Rapoport, "Laboratory Text in Organic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1950, pp. 237–45). Infrared spectra were determined on a Baird double beam recording spectrophotometer or a Perkin-Elmer Model 21 recording spectrophotometer, using thin films or a solution in carbon tetrachloride; solutions in carbon tetrachloride, carefully prepared under anhydrous conditions and measured in 0.1 mm. cells on the Baird machine, were used for the data recorded in Fig. 1. Microanalyses were by the Microanalytical Division, Department of Chemistry, University of California, Berkeley.

Distillation yielded, after a small forerun, an 82% yield of colorless product, b.p. 61°/5 mm. The carbonyl peak was at 5.57 μ .

10-Ketohendecanoyl chloride was prepared as a reference sample of a keto acid chloride which must exist as the open chain compound. A minimum of heating is required for successful preparation of this compound. A mixture of 1.0 g. of 10-keto-hendecanoic acid²⁶ and 1.5 ml. of purified thionyl chloride was kept at room temperature for 4 hr., then excess thionyl chloride was removed under reduced pressure. The residue was evaporatively distilled at 80° and 0.5 mm. pressure, to give a colorless sample used for infrared spectra. Carbonyl peaks were observed at 5.55 μ and at 5.85 μ .

Levulinyl chloride was prepared by the procedure of Langlois and Wolff,²¹ by adding 60 g. of purified thionyl chloride dropwise to 50 g. of levulinic acid, as the temperature was maintained below 50°. Since this acid chloride is quite heat sensitive, the excess thionyl chloride was removed at reduced pressure and temperatures below 50°, then 10 ml. of dry benzene was added and removed at reduced pressure. After an additional 10-ml. portion of benzene had been added and carefully removed, the residual acid chloride was used for determination of the infrared spectrum (or in chemical reactions). There was a single well defined carbonyl band²² at 5.54 μ .

γ -Ketocaproyl chloride. *Ethyl γ -ketocaproate* was prepared from diethylcadmium and β -carbethoxypropionyl chloride essentially according to the procedure which has been described²⁸ for preparation of propiophenone. The yield of ester boiling sharply at 93°/9 mm. was 55%, n_D^{21} 1.4257 (lit.,²⁷ b.p. 106°/16 mm.). A 20-g. sample of ester was saponified by heating on a steam bath for 2 hr. with 160 ml. of aqueous 10% sodium hydroxide. The cooled homogenous solution was continuously extracted with ether for 12 hr. to remove any neutral material, then it was acidified to Congo Red and the keto acid was continuously extracted with ether. Removal of ether at reduced pressure from the dried solution left 15.5 g. of γ -ketocaproic acid which was used directly for preparation of the acid chloride according to the procedure described above for levulinyl chloride.

δ -Ketoanthyl chloride. *Methyl δ -ketoanthate* was prepared from diethylcadmium and γ -carbomethoxybutyryl chloride by the procedure used for the γ -ketocaproate. The yield was 82% of material of b.p. 108–109°/14 mm., n_D^{25} 1.4284, carbonyl bands at 5.75 μ and at 5.81 μ (lit.,²⁸ b.p. 130°/20 mm.). The ester was saponified as described for the γ -ketocaproate, to give 92% yield of the keto acid, which had m.p. 48.0–48.5° after crystallization from hexane (lit.,²⁹ m.p. 50°).

(26) J. Cason, *J. Am. Chem. Soc.*, **68**, 2078 (1946).

(27) M. Maire, *Bull. soc. chim. France*, [4], **3**, 285 (1908).

(28) B. W. Clutterbuck and H. S. Raper, *Biochem. J.*, **19**, 385 (1925).

(29) E. E. Blaise and M. Maire, *Bull. soc. chim. France*, [4], **3**, 424 (1908).

Anal. Calcd. for $C_7H_{12}O_3$: C, 58.31; H, 8.39; equiv. wt., 144. Found: C, 58.36; H, 8.13; equiv. wt., 142.

The keto acid chloride was prepared as described for levulinyl chloride, but this compound may be distilled with some decomposition at reduced pressure. The yield of colorless distilled product was 40%, b.p. 65°/4 mm. The infrared spectrum, in carbon tetrachloride solution, of either distilled or undistilled keto acid chloride showed carbonyl absorption at 5.65 μ . A minor band (of variable intensity in different samples) at 5.94 μ could never be eliminated, even with undistilled samples. Analysis for chlorine gave 12.6% (theory for $C_7H_{11}O_2Cl$, 21.8%).

γ -Ethyl- γ -formylcaprylyl chloride. A mixture of 20 g. (0.11 mole) of γ -ethyl- γ -formylcaprylic acid¹¹ and 26.2 g. (0.22 mole) of purified thionyl chloride was allowed to react (most favorable conditions) for 30 min. at room temperature, followed by 30 min. at 40°, then excess thionyl chloride was removed at reduced pressure. Distillation of the residue in a Claisen flask yielded 18.7–19.0 g. (86–87%) of slightly yellow product, b.p. 128–130°/2 mm. In one run in which distillation was in the half-meter column, the yield of colorless product of the same b.p. was 17 g. When phosphorus pentachloride was used for the preparation, the yield of a yellow product was only 52%. The infrared spectrum showed three carbonyl peaks, at 5.59, 5.67, and 5.83 μ , the center peak being the stronger and the side peaks of nearly equal intensity.

Ethyl γ -ethyl- γ -formylcaprylate. A 5-g. portion of γ -ethyl- γ -formylcaprylyl chloride was added dropwise to a large excess of anhydrous ethanol. After the reaction mixture had stood for 2 hr., excess ethanol was removed by distillation and the product distilled to yield 3.7 g. (71%) of ester of b.p. 110°/1.5 mm., n_D^{25} 1.4432. Infrared absorption at 3.70 μ is attributed to hydrogen on carbonyl, while the single band at 5.79 μ is regarded as due to both aldehyde and ester carbonyl.

Anal. Calcd. for $C_{13}H_{24}O_3$: C, 68.37; H, 10.60 Found: C, 68.83; H, 10.72.

γ -Ethyl- γ -formylcaprylamide. (A). A 1.1-g. sample of γ -ethyl- γ -formylcaprylyl chloride was added to 10 ml. of ice cold concentrated aqueous ammonium hydroxide, with shaking. The white solid, which separated at once, weighed 0.7 g. and had m.p. 135–140° (gas evolution). After three crystallizations from butanone, the amide had m.p. 159–160° (gas evolution), varying somewhat with rate of heating.

Anal. Calcd. for $C_{11}H_{21}O_2N$: C, 66.28; H, 10.62; N, 7.02. Found: C, 66.65; H, 10.50; N, 7.05.

(B). A solution of 1.4 g. of γ -ethyl- γ -formylcaprylonitrile in 5 ml. of 15% alcoholic potassium hydroxide was boiled for 15 min., then poured into 20 ml. of water. An oil separated, which crystallized on standing for several hours, weight 0.2 g. After crystallization from butanone, the substance had m.p. 158–160° (gas evolution), and there was no depression in melting point when this sample was mixed with that prepared from the acid chloride.

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