solution of 30 g. of 2-aminopyridine in 125 cc. of 40% fluoboric acid was diazotized by the addition of 22.5 g. of sodium nitrite, the solid being added slowly in small portions with vigorous stirring. Since the diazonium salt decomposes almost immediately with liberation of heat, it is necessary to add the sodium nitrite slowly to keep the temperature below 10°. After an hour of standing in the ice-bath, the solution was warmed to 37° to complete the decomposition. A dark oil separated when the solution, cooled to 5°, was neutralized with sodium carbonate; the solution was steam-distilled and the 2-fluoropyridine was separated from the water layer; ether extraction at this point is not advisable because much of the product is lost on evaporation of the ether. When dried over sodium sulfate and distilled at 758 mm., the product (10.6 g., 34.2%) boiled at 125°; n^{20}_D 1.4674 (*cf.* ref. (5), b. p. 125.8° (752 mm.); n^{20}_D 1.4678). Decomposition of 2-fluoropyridine was indicated by the appearance of a yellow color after several days, and the formation of a white precipitate on longer standing.

3-Fluoropyridine.—The following procedure was the best of several tried: 12.5 g. of 3-aminopyridine was dissolved in a mixture of 50 cc. of 40% fluoboric acid and 100 cc. of 95% ethanol. The solution was cooled to 0° and a stream of ethyl nitrite[9] was passed in until no more of the diazonium fluoborate precipitated. Fifty cc. of cold ether was added to complete the precipitation, and the mixture was filtered while cold, washed once with cold ether and then once with cold petroleum ether. Care was taken not to allow the precipitate to become completely dry, for the dry diazonium salt will undergo spontaneous decomposition. The salt was then dampened with petroleum ether and transferred to a beaker containing cold high-boiling petroleum ether. The temperature of the mixture was kept below 25°; above this point the decomposition is uncontrollable, whereas from 15–25° the decomposition takes place slowly.

After the decomposition was complete a few cc. of conc. hydrochloric acid was added to assure salt formation, and the solvent removed under reduced pressure. The residue was made alkaline with sodium hydroxide solution, keeping the solution cold during the process. The solution was then distilled, and solid sodium hydroxide added to the distillate, whereupon an oil separated. The oil was dried with sodium hydroxide; the resulting 3-fluoropyridine boiled at 105–107° (752 mm.), n^{20}_D 1.4700 (*cf.* ref. (6), b. p. 106–108° (750 mm.)). The yield so obtained was 6.2 g. (48%); another 0.2 g. was recovered by reworking the mother liquor, bringing the total yield to 50%.

4-Fluoropyridine.—Methods similar to the ones which proved successful in the preparation of 2- and 3-fluoropyridine were tried without success. Diazotization of 4-aminopyridine appeared to take place rapidly at 0°; the fluoborate of the amine is less soluble than the diazonium fluoborate, so the precipitate dissolved as the diazotization progressed. When the diazotized solution was warmed to about 15° decomposition began, as evidenced by the evolution of nitrogen. When the decomposed diazotized solution was neutralized a red oil appeared, which turned more or less rapidly to a brown solid. When the neutralized solution was distilled the distillate had a pyridine-like odor which disappeared rapidly, the solution becoming amber in color. Treatment of any of the decomposition products with picric acid produced a solid picrate, m. p. 193–195°. This agrees with the melting point reported[7] for the picrate of N-(4′-pyridyl)-4-pyridone.

Summary

2-Fluoropyridine has been prepared in 34% yield and 3-fluoropyridine in 50% yield from the corresponding amines by the Schiemann reaction. Attempts to isolate the unstable 4-fluoropyridine by this method were unsuccessful.

CHAPEL HILL, NORTH CAROLINA RECEIVED MAY 14, 1947

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(9) Semon and Damerell, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 204.

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Ketene Dimers from Acid Halides

BY J. C. SAUER

Diketene, the first member of the ketene dimer series, is readily prepared in good yield by dimerizing ketene.[1] However, no satisfactory method for the synthesis of monosubstituted ketenes[2] ($RCH{=}C{=}O$) and, accordingly, the dimers from them, has been reported. The dehydrohalogenation of acid chlorides, either by pyrolysis[3] or by means of aliphatic tertiary amines,[4] has given low yields of ketene trimers. In the latter case, 2,4-pyranones were obtained but ketene dimers were not identified.

This paper describes a practical synthesis of dimers of monoalkyl ketenes.[5] The reaction involves the dehydrohalogenation of acid halides of the type RCH_2COX by aliphatic tertiary amines. The dehydrohalogenation of the acid halide is assumed to involve the formation of an intermediate ketene monomer which rapidly undergoes self-addition, probably under the catalytic influence of tertiary amine and tertiary amine hydrohalide, as indicated in the equations[6]

$$RCH_2COX + R'_3N \longrightarrow [RCH{=}C{=}O] + R'_3N{\cdot}HX$$

$$2[RCH{=}C{=}O] \longrightarrow RCH_2COCR{=}C{=}O$$

No evidence for the transitory existence of the ketene monomers was obtained, the lowest boiling product isolated in every case being the dimer.

The dehydrohalogenations were usually carried out by adding an equivalent amount of tertiary

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(1) Boese, *Ind. Eng. Chem.*, **32**, 16 (1940).

(2) Hurd, Cashion and Perletz, *J. Org. Chem.*, **8**, 367 (1943); **9**, 557 (1944).

(3) Bistrzycki and Landtwing, *Ber.*, **42**, 4720 (1909).

(4) Wedekind, *ibid.*, **34**, 2070 (1901); *Ann.*, **323**, 246 (1902); *ibid.*, **378**, 261 (1910); Wedekind and Haeussermann, *Ber.*, **41**, 2297 (1908).

(5) Sauer, U. S. Patent 2,369,919; Adams, "Organic Reactions," Vol. III, p. 129 (1946).

(6) The dimers are represented as having linear structures for the purposes of this paper. For leading references dealing with the structure of diketene, the first member of the ketene dimer series, see Taufen and Murray, THIS JOURNAL, **67**, 754 (1945); Rice and Roberts, *ibid.*, **65**, 1677 (1943); Hurd and Abernethy, *ibid.*, **62**, 1147 (1940); and ref. 1.

amine to a solution of the acid halide in an inert solvent such as ether, benzene or carbon tetrachloride. Adding the acid halide to a solution of the base was equally satisfactory. Tertiary aliphatic or tertiary cycloaliphatic amines were found to be suitable bases for the dehydrohalogenation. However, N,N-dimethylaniline or pyridine, even at elevated temperatures and superatmospheric pressures, did not bring about the desired reaction. The reactants were usually mixed at room temperature and the reaction was complete, as judged by disappearance of acid halide, in one to three hours. Dehydrohalogenation apparently was complete within a few minutes at elevated temperatures, such as in refluxing toluene. The yields of isolated ketene dimers ranged from 40–100%. In those cases where the dimers were not isolated from the reaction mixture but were converted to derivatives, yields based on derivatives generally ranged from 70–100%. Table I summarizes the results obtained in the dehydrohalogenation of twelve acid chlorides and bromides. The experimental section gives detailed directions for the synthesis of representative dimers.

These dimers have many of the chemical properties attributed to the ketene group and are useful reagents for the synthesis of β-keto acid derivatives,[7] as indicated schematically below.

$$RCH_2COCR{=}C{=}O\text{—}\begin{cases}\xrightarrow{R'OH} RCH_2COCHRCO_2R' \\ \xrightarrow{R'NH_2} RCH_2COCHRCONHR' \\ \xrightarrow{H_2O} RCH_2COCHRCO_2H \xrightarrow[\Delta]{-CO_2} (RCH_2)_2CO\end{cases}$$

An interesting application of the hydration reaction involves the dehydrohalogenation and ketonization of 5-carbomethoxyvaleryl chloride (I) to 6-ketohendecane-1,11-dioic acid (II) in an over-all yield of 70% according to the scheme

$$\underset{(I)}{CH_3O_2C(CH_2)_4COCl} + R_3N \longrightarrow$$

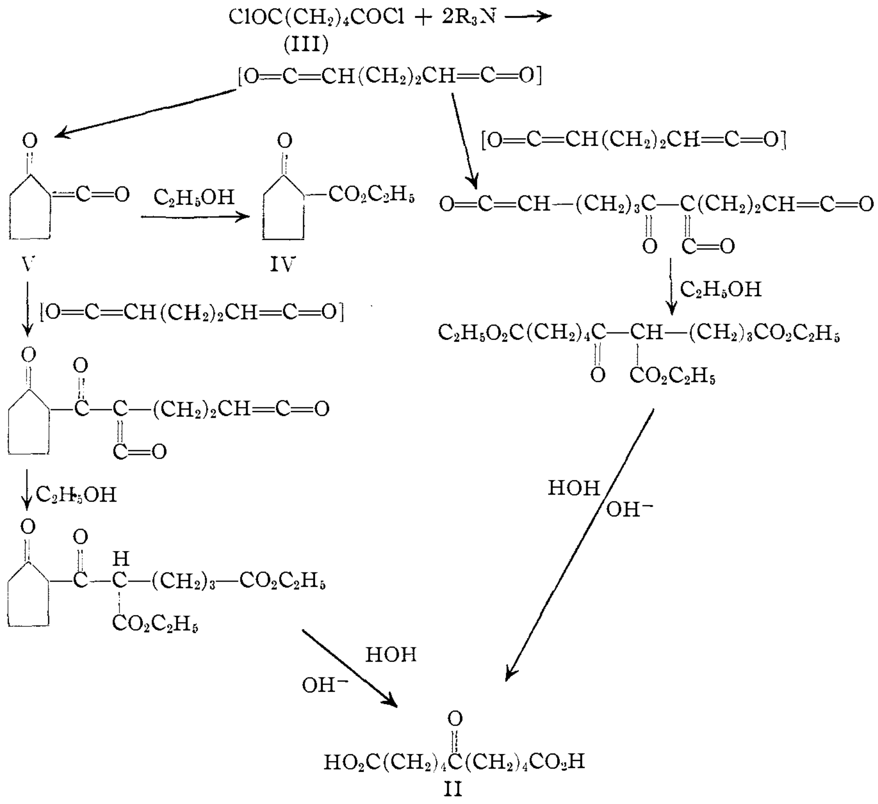
$$CH_3O_2C(CH_2)_4COC[(CH_2)_3CO_2CH_3]{=}C{=}O \xrightarrow[(NaOH)]{HOH}$$

$$NaO_2C(CH_2)_4COCH[(CH_2)_3CO_2Na]CO_2Na \xrightarrow[-CO_2]{H^-}$$

$$\underset{(II)}{HO_2C(CH_2)_4CO(CH_2)_4CO_2H}$$

The dehydrohalogenation of a mixture of two acid chlorides should lead to the formation of a mixture of four ketene dimers[5,8] on the basis of the assumption that two monomeric ketenes would first be formed. The monomers would subsequently undergo self-addition to form the usual dimers and also addition to one another to form unsymmetrical, mixed dimers. In the dehydrohalogenation of a mixture of acetyl and lauroyl chlorides, the formation of the two simple dimers and one of the mixed dimers ($C_{11}H_{23}CO$-$CH{=}C{=}O$) was demonstrated by reaction with aniline to form the corresponding acetoacetanilides. The presence or absence of the other theoretically possible mixed dimer ($CH_3COC(C_{10}H_{21}){=}C{=}O$) was not established. Similar results were obtained in the dehydrohalogenation of a mixture of propionyl and caproyl chlorides.

Staudinger[9] reported that adipyl chloride (III) was dehydrochlorinated to yield the product $[O{=}C{=}CH(CH_2)_2CH{=}C{=}O]_2$, the structure of



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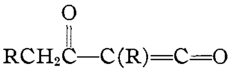
[7] Sauer, U. S. Patent 2,323,938.

[8] Sauer, U. S. Patent 2,238,826.

[9] Staudinger, "Die Ketene," Ferdinand Enke, Stuttgart, 1912, p. 19.

TABLE I

KETENE DIMERS 

$RCH_2\overset{\overset{\displaystyle O}{\|}}{C}—C(R)=C=O$

R	Prepared from	Solvent	Yield, %	B. p. (mm.) or m. p.[c]	$n^{25}D$
H	Acetyl chloride	Ether	50	96 (400)	....
H	Acetyl bromide	Ether	40	96 (400)	....
CH_3	Propionyl chloride	Ether	74	57–58 (12)	1.4280
C_2H_5	*n*-Butyryl chloride	Ligroin	70	95–96 (32)	1.4387
n-C_3H_7	*n*-Valeryl chloride	Ligroin	93[a]	135 (30)	1.4433
Iso-C_3H_7	Isovaleryl chloride	Ether	56.5[b]	108–110 (35)	1.4343
C_4H_9	Caproyl chloride	Ligroin	40	127–129 (10)	1.4478
C_6H_{13}	Capryloyl chloride	Ether	56	132–133 (2)	1.4489
$C_{10}H_{21}$	Lauroyl chloride	Ether	100	41–42	....
$C_{12}H_{25}$	Myristoyl chloride	Ligroin	....	42–44	....
$C_{16}H_{33}$	Stearoyl chloride	Benzene	100	62–63	....
$C_{16}H_{33}$	Stearoyl bromide	Ether	83	....	....

which was not determined. We have found that adipyl chloride (III) undergoes dehydrohalogenation quantitatively but the product, after separation from amine salt, resinified when distillation was attempted. However, when the dehydrohalogenation product, without isolation from the solvent, was treated with ethanol, a 40% yield of ethyl 2-cyclopentanonecarboxylate (IV) was obtained. It is believed that the difunctional monomeric ketene, first formed, underwent cyclization in part to yield (α-ketotetramethylene)-ketene (V), which in turn reacted with ethanol to give ethyl 2-cyclopentanonecarboxylate (IV), as indicated schematically below. A low yield of 6-ketohendecane-1,11-dioic acid (II) was obtained by alkaline hydrolysis of the residual non-volatile material.

Sebacyl chloride, on the other hand, was converted to a polymeric ketene derivative. Recently sebacyl chloride has been dehydrohalogenated under conditions of high dilution to form a macrocyclic diketene.[10]

Experimental

Materials

The acyl halides, other than reagent-grade shelf chemicals, were made from the acids and thionyl chloride. The highest yields of stearoyl chloride were obtained by allowing molecular equivalents of triple-pressed stearic acid and thionyl chloride to react slowly at room temperature for forty-eight hours and then warming two to three hours on the steam-bath. The crude acid chloride was distilled in small portions in a 125-ml. Claisen flask which was nearly completely immersed in heat exchange oil. In this manner, up to 86% yields of stearoyl chloride, boiling at 150° (1 mm.), (reported[11] 165° (0.4 mm.)) were isolated.

Stearoyl bromide was prepared by adding phosphorus tribromide to triple-pressed stearic acid according to the procedure used for preparing phenylacetyl chloride.[12] The crude stearoyl bromide was distilled in the same way as the stearoyl chloride and a 10% yield of product boiling at 172–178° (1 mm.) was obtained. Triethylamine purchased from the Eastman Kodak Company was purified by drying over caustic followed by distillation from 10% of its weight of α-naphthyl isocyanate. Trimethylamine was obtained from the Organic Chemicals Department of the du Pont Company and used without further purification.

Synthesis of Ketene Dimers and Derivatives.—Typical directions for the synthesis of representative ketene dimers and derivatives are given below. Melting points and boiling points are uncorrected.

Hexadecylketene Dimer.—Into a dry, 500-ml. Erlenmeyer flask was poured 225 ml. of anhydrous benzene and 15 g. (0.05 mole) of stearoyl chloride, b. p. 150° (1 mm.). The solution was seeded with 0.5 g. of triethylamine hydrochloride.[13] To this solution was added 6 g. (0.06 mole) of triethylamine at room temperature. The flask was tightly stoppered and set aside for sixteen hours. The solution of the ketene dimer was separated from the amine salt by the inverted filtration method.[14] The washed, air-dried hydrochloride weighed 7.4 g. (100%). The filtrate was concentrated on a steam-bath *in vacuo* and the residue taken up in hot ligroin. Upon cooling, 12 g. (90.3%) of hexadecylketene dimer melting at 62–63° was obtained.

Methylketene Dimer.—Into a 2-liter, three-necked round-bottomed flask equipped with a reflux condenser carrying a calcium chloride tube, a motor-driven stirrer with a mercury seal, and a 250-ml. dropping funnel was poured 980 ml. of anhydrous ether. The solvent was seeded with 1 g. of triethylamine hydrochloride. Stirring was commenced and 179 g. (1.9 moles) of propionyl chloride, b. p. 79–80°, was added rapidly through the condenser. To the agitated mixture was added dropwise from the funnel 202 g. (2.0 moles) of triethylamine, b. p. 88°, at a rate sufficient to maintain refluxing. The addition of amine required one hour, during which the triethylamine hydrochloride precipitated as a cream-colored solid. The reaction mixture was stirred for one hour after the addition of the triethylamine and was then allowed to stand overnight at room temperature.

The solution of the ketene dimer was separated from the precipitated amine salt by the inverted filtration method. The ether was removed from the filtrate by fractionation through a helix-packed column (2.5 cm. by 90 cm.). The light yellow residue which remained was transferred to a modified Claisen flask and distilled. The methylketene dimer boiled at 57–58° (12 mm.) and

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[10] Blomquist and Spencer, THIS JOURNAL, **69**, 472 (1947).

[11] Averill, Roche and King, *ibid.*, **51**, 866 (1929).

[12] Allen and Barker, "Organic Syntheses," **12**, 16 (1932).

[13] In some cases the tertiary amine salt precipitated from the reaction mixture as a gelatinous mass which made subsequent filtration slow and difficult. To avoid this difficulty, the solvent was seeded with tertiary amine salt before carrying out the dehydrohalogenation. Completeness of reaction was conveniently determined by withdrawing a sample of the reaction mixture, filtering, and adding aniline to the filtrate; the dehydrohalogenation was judged complete if no precipitation of aniline hydrohalide was observed.

[14] Bost and Constable, "Organic Syntheses," **16**, 81 (1936).

TABLE I (*Continued*)

Percentage composition						Derivative			
Calcd.			Found			Ketone B. p. (mm.) or m. p.[e]	Anilide		
							M. p.[g,h]	Percentage composition Calcd.	Found
C	H	M. W.	C	H	M. W.[d]			N	N
..	..	...	..	..	...	........[f]	83–84[i]	...	...
..	..	...	..	..	...	....	83–84[i]	...	...
64.3	7.2	112	63.9	7.3	114	....	.....	...	...
68.5	8.6	140	66.3	8.8	136	....	84–85	6.0	6.2
..	..	168	..	..	164	182–183	68–69	5.4	5.6
..	..	168	..	..	163	48–51 (32)	105–106	5.4	5.7
..	..	196	..	..	198	....	76–77	4.8	5.0
76.2	11.1	252	76.3	11.2	235	41	80–82	4.1	4.1
79.1	12.1	364	78.9	12.2	351	69	84–85	3.1	3.2
80.0	12.4	...	80.1	12.6	...	74–75	82	2.7	2.8
81.1	12.7	532	80.3	12.3	494	86–87	77–78	2.2	2.5
..	..	...	..	..	...	....	77–78	2.2	2.5

[a] The reaction mixture was divided into two parts from which were isolated, respectively, a 20% yield of *n*-propylketene dimer, and a 73% yield of 5-nonanone (after ketonization). The recorded yield is the sum of the yields of dimer and ketone. [b] From a portion of the reaction mixture was isolated a 20% yield of isopropylketene dimer and the remainder was converted into 2,6-dimethyl-4-heptanone (18.5%) and ethyl α-isovalerylisovalerate (18%), b. p. 118–119° (15 mm.) (recorded b. p. is 118–119° (15 mm.) in Adams, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, 1942, p. 288). The recorded yield is the sum of yields for dimer and derivatives. [c] Boiling points and melting points are uncorrected. [d] Molecular weights were determined cryoscopically in inert solvents such as benzene or dioxane except in the case of decylketene dimer, which was determined by saponification. [e] Some recorded values for ketones listed in this column are as follows: 5-nonanone, 187.6°, in Timmermans, *Bull. Soc. Chim. Belg.*, **36**, 502 (1927); 2,6-dimethyl-4-heptanone, 166°, in Skita, *Ber.*, 41, 2938 (1908); 8-pentadecanone, 40° in ref. 17; 12-tricosanone, 69°, in Krafft, *Ber.*, 15, 1711 (1882); 14-heptacosanone, 72.3°, in previous ref.; 18-pentatriacontanone, 88.4°, in previous ref. [f] Isolated as dibenzal derivative, m. p. 108° (recorded m. p. is 110–111° in Blatt, "Organic Syntheses," Coll. Vol. II, p. 167, John Wiley & Sons, Inc.). [g] Anilides were purified by recrystallization from absolute or dilute ethanol. [h] In some cases unsubstituted amides were prepared by passing ammonia into an ether solution of the dimer. The amide from methylketene dimer melted at 83–84° (recorded m. p. is 82° in Pingel, *Ann.*, **245**, 84 (1888)). The amide from hexylketene dimer melted at 109–110°. *Anal.* Calcd. for $C_{16}H_{31}O_2N$: N, 5.1. Found: N, 5.1. The amide from decylketene dimer melted at 114–115° (recorded m. p. is 114–115° in McCorkle, *Iowa State Coll. J. Sci.*, **14**, 64 (1939)). The amide of hexadecylketene dimer melted at 104° (compound recorded by McCorkle in above reference but constants not given). *Anal.* Calcd. for $C_{36}H_{71}O_2N$: N, 2.5. Found: N, 2.2. [i] Recorded m. p. is 84–85° in Kotz, *J. prakt. Chem.*, [2] **103**, 240 (1921). A mixed m. p. with an authentic sample showed no depression.

weighed 75 g. (70.5%). Methylketene dimer is a colorless, oily liquid, fumes of which are mildly irritating to the nostrils.

Ethyl α-Propionylpropionate from Methylketene Dimer.—In a 100-ml. round-bottomed flask attached to a reflux condenser holding a calcium chloride drying tube was placed 32 g. (0.7 mole) of absolute ethanol. To this 10 g. (0.09 mole) of methylketene dimer was added through the condenser. After the mixture had stood several hours the excess ethanol was removed by distillation. Distillation of the residue yielded 9.2 g. (65%) of ethyl α-propionylpropionate boiling at 85–86° (11 mm.), (reported[15] 88–90° (12 mm.)).

Ethyl α-Capryloylcaprylate.—Into a 2-liter, three-necked round-bottomed flask equipped with a reflux condenser carrying a calcium chloride tube, a motor-driven stirrer with a mercury seal, and a jacketed graduated dropping funnel of 100-ml. capacity was poured a solution containing 145 g. (0.89 mole) of capryloyl chloride, b. p. 80° (15 mm.), in 640 ml. of anhydrous ligroin. The jacketed funnel was fitted with a soda-lime tube and was cooled by circulating methanol which was refrigerated in a bath of Dry Ice and methanol, and 76 ml. (53 g., 0.9 mole) of trimethylamine was condensed into it. The acid chloride solution in the flask was cooled to 0° and the trimethylamine was added in a fine stream with vigorous stirring during a period of ten minutes. The reaction mixture was then allowed to warm to room temperature. After five hours, 200 ml. of absolute ethanol containing 5 ml. of concentrated sulfuric acid was added to the reaction mixture. After sixteen hours at room temperature, 500 ml. of water was added to the mixture, and the oily layer was separated, washed with water, 2% hydrochloric acid, 2% sodium carbonate, and finally with water. After drying over anhydrous magnesium sulfate, the ligroin was separated by distillation and the residue was distilled in a helix-packed column (1.5 cm. by 30 cm.). The ethyl α-capryloylcaprylate boiling at 161–165° (4 mm.) (reported[16] 161° (4 mm.)) weighed 92 g. (70%), n^{29}_{D} 1.4408.

8-Pentadecanone.—Capryloyl chloride (15.1 g., 0.093 mole) in 160 ml. of ether was converted into hexylketene dimer according to the procedure outlined above. The reaction mixture was filtered and 3 g. (0.16 mole) of water was added to the filtrate. The ether was removed by warming over a steam-bath. From the residue was obtained 10 g. of 8-pentadecanone (95%) melting at 41° (reported[17] 40°) after one recrystallization from ethanol.

6-Ketohendecane-1,11-dioic Acid.—Into equipment similar to that used for the synthesis of methylketene dimer was charged 200 ml. of ether and 17.8 g. (0.1 mole) of 5-carbomethoxyvaleryl chloride, b. p. 112–113° (13 mm.). To this solution was added rapidly with stirring 10.3 g. (0.1 mole) of triethylamine. The mixture was refluxed for a few minutes and then allowed to stand at room temperature for two days. The amine salt (13.8 g., 100%) was isolated by filtration on a Buchner funnel and the ether was removed from the filtrate by warming over a steam-bath. The residue was mixed with a solution containing 18 g. (0.32 mole) of potassium hydroxide in 100 ml. of 90% ethanol and refluxed four hours. The alcohol was then largely removed by evaporation over a steam-bath. After cooling, the alkaline solution was extracted once with ether to remove traces of insoluble impurities, acidified to congo red by addition of dilute hydrochloric acid, and the acid solution evaporated to a volume of about 50 ml. Upon cooling, crystals of crude

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[15] McElvain, THIS JOURNAL, **51**, 3124 (1929).

[16] Briese and McElvain, *ibid.*, **55**, 1697 (1933).

[17] Guckelberger, *Ann.*, **69**, 201 (1849).

6-ketohendecane-1,11-dioic acid precipitated. The product was filtered and a second crop of crystals obtained by further concentration of the mother liquor. The combined crops of crystals were purified by dissolving in boiling water containing Norit, filtering hot, and cooling. A second recrystallization from boiling water gave 7.6 g. (67%) of pure acid melting sharply at 109°.

Anal. Calcd. for $C_{11}H_{18}O_5$: C, 57.3; H, 7.8; neut. equiv., 115.0. Found: C, 57.2; H, 7.8; neut. equiv., 114.8.

The semicarbazone of this keto acid, after recrystallization from water, melted at 194–195°.

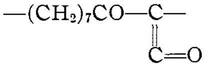
Anal. Calcd. for $C_{12}H_{21}O_5N_3$: N, 14.6. Found: N, 14.3.

Ethyl 2-Cyclopentanonecarboxylate from Adipyl Chloride.—Adipyl chloride (283 g., 1.55 moles) in 1700 ml. of benzene was quantitatively dehydrohalogenated by 318 g. (3.10 moles) of triethylamine using the procedure described for the synthesis of methylketene dimer. The solution containing the dehydrohalogenation product was separated from the precipitated amine salt by inverted filtration. To the benzene solution was added 350 ml. (6.0 moles) of ethanol containing a trace of anhydrous hydrogen chloride. The benzene was removed by fractionation through a helix-packed column (2.5 cm. by 90 cm.). The yellow residue which remained was then fractionated through the same column and 98.0 g. (40%) of ethyl 2-cyclopentanonecarboxylate boiling at 103–104° (11 mm.) (reported[18] 103–104° (11 mm.)) was collected.

The semicarbazone of ethyl 2-cyclopentanonecarboxylate melted at 142–144° (reported[19] 143°).

From the residue which remained in the distillation flask was obtained an undetermined but low yield of 6-ketohendecane-1,11-dioic acid, m. p. 108–109°, by alkaline hydrolysis. A mixed melting point determination with a sample prepared by dehydrohalogenating 5-carbomethoxyvaleryl chloride showed no depression.

Polymeric Ketene from Sebacyl Chloride.—A solution of 14.8 g. (0.062 mole) of sebacyl chloride in 250 ml. of ether was dehydrohalogenated with 13 g. (0.13 mole) of triethylamine at 0°. After twenty-four hours at room temperature the precipitate was separated by filtration. The solvent was removed from the filtrate by distillation and there remained a residue consisting of 3 g. of a waxy ketene polymer having a molecular weight of 1400 (cryoscopic determination in dioxane). An additional 5 g. of polymer of molecular weight 1700 separated from the reaction mixture along with the triethylamine hydrochloride, from which it was extracted with hot dioxane. A precipitate was formed when ammonia was passed into the dioxane solution of the polymer. This precipitate, after filtering and air-drying, was found to contain 4.25% nitrogen. Assuming that this polymeric ketene contained the structural unit



$$—(CH_2)_7CO—\underset{\underset{\displaystyle C{=}O}{\|}}{C}—$$

complete amidation would have given a polymer containing 7.6% nitrogen.

Dehydrohalogenation of a Mixture of Acetyl and Lauroyl Chlorides.—A mixture of 11.7 g. (0.15 mole) of acetyl chloride and 39.3 g. (0.18 mole) of lauroyl chloride was dehydrohalogenated in benzene with triethylamine. After removing the triethylamine hydrochloride by filtration, 19 g. (0.2 mole) of aniline was added to the filtrate. After standing twenty hours at room temperature, the solvent was evaporated and the residue fractionally crystallized from alcohol. The formation of the symmetrical dimers was proved by the isolation of 16.8 g. (40%) of α-lauroyllauranilide melting at 84–85° and 4 g. (30%) of acetoacetanilide melting at 83–84°. There was also obtained 4 g. (9%) of lauroylacetanilide melting at 54–57°. This compound was distinguished from the isomeric α-acetolauranilide as follows: the anilide (1.7 g.) obtained from the mixed dimer was coupled with *p*-nitrobenzenediazonium chloride in 50% dioxane solution at 10° to give a red dye melting at 84–85° after recrystallization from 95% ethanol (2.2 g., 88%). Under identical conditions, α-acetolauranilide, synthesized by established procedures, did not couple with the diazonium chloride. *p*-Nitrosodimethylaniline was coupled with the anilide prepared from the mixed dimer to give a yellow dye, whereas this color test was negative in the case of α-acetolauranilide.

Anal. of lauroylacetanilide. Calcd. for $C_{20}H_{31}O_2N$: N, 4.5. Found: N, 4.6.

Anal. of α-(*p*-nitrophenylazo)-lauroylacetanilide. Calcd. for $C_{26}H_{34}O_4N_4$: N, 12.0. Found: N, 12.0.

Dehydrohalogenation of a Mixture of Propionyl and Caproyl Chlorides.—A mixture of 69.4 g. (0.75 mole) of propionyl chloride and 86.0 g. (0.64 mole) of caproyl chloride, b. p. 151–152°, was dehydrohalogenated in petroleum ether with triethylamine. The ketene dimer mixture was fractionated to yield the following products: 14.9 g. (36%) of methylketene dimer boiling at 70–75° (30 mm.), 22 g. (23%) of a mixed ketene dimer boiling at 111–116° (30 mm.), and 17 g. (27%) of butylketene dimer boiling at 135–148° (30 mm.).

Anal. of mixed ketene dimer. Calcd. for $C_9H_{14}O_2$: C, 70.1; H, 9.1; mol. wt., 154. Found: C, 69.3; H, 9.8; mol. wt., 144.

By passing gaseous ammonia into an ethereal solution of the mixed dimer, there was obtained a precipitate which melted at 102–103° after recrystallization from ethanol. This amide could have been either α-caproylpropionamide ($CH_3CH(C_5H_{11}CO)CONH_2$) or α-propionylcaproamide ($C_4H_9CH(C_2H_5CO)CONH_2$), or a mixture of them.

Anal. Calcd. for $C_9H_{17}O_2N$: N, 8.2. Found: N, 8.3.

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Summary

Dimers of monoalkylated ketenes have been prepared by dehydrohalogenating acid halides of the type RCH_2COX by means of aliphatic tertiary amines. When a mixture of two acid chlorides was dehydrohalogenated, mixed ketene dimers were formed in addition to the symmetrical dimers. In extension of the dehydrohalogenation to dibasic acid chlorides, it was found that sebacyl chloride gave a polymeric ketene derivative, presumably by intermolecular addition, while the ketene from adipyl chloride underwent cyclization to yield principally (α-ketotetramethylene)-ketene.

The dimers have many of the chemical properties attributed to the ketene group and are useful reagents in the synthesis of β-keto acid derivatives.

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