distilled to remove the solvent. A small amount of biphenyl (0.1 g.) was recovered. It melted at 69–71° and showed no depression when mixed with an authentic sample.

Thermal decomposition of the potassium compounds. A suspension (50 ml.), containing 28.2 milliequiv. of phenylpotassium in heptane-benzene, was centrifuged and washed with pentane in order to remove all trace of benzene or biphenyl. Then the pentane was removed by vacuum distillation and the phenylpotassium was subjected to heat at 150°/1 mm. for 9 hr. The solid collected in the cold trap melted to a liquid with the odor of benzene. The yield was 1.06 g. (50%); n_D^{25} 1.4960. The residue from this decomposition was decomposed with methanol. The product was infusible and insoluble in common organic solvents. An analysis showed 87.03% carbon and 4.85% hydrogen with some ash. The atomic ratio of 1.5 carbon for each hydrogen atom suggests that a condensed aromatic system was present. The infrared absorption made on a sodium bromide pellet was pronounced at 1600 cm.$^{-1}$ and at 695 to 810 cm.$^{-1}$, characteristic for substituted benzene rings.

A similar decomposition was carried out on the reaction product of phenylpotassium with benzene. An aged suspension (50 ml.) containing 41.7 milliequiv. of phenylpotassium or its equivalent was centrifuged and washed with pentane. From this material 1 g. (30% yield) of a white powder was collected at 150°/1 mm. It was identified as biphenyl by its melting point (70°) and mixed melting point with an authentic sample. The residue was not soluble in benzene and common solvents and appeared similar to that obtained from phenylpotassium itself.

Potassium metal with biphenyl. Biphenyl (78 g., 0.5 mole) was stirred with 39 g. (1 atom) of potassium sand in 500 ml. of heptane at 70° for 6 hr. The infrared absorption bands of this suspension were identical with those from a fully aged preparation of phenylpotassium with benzene. After carbonation 61 g. (50%) of carboxylic acids was recovered which melted at 240–250°. The infrared absorption of these acids was the same as for the acids derived from the reaction of phenylpotassium with benzene. The melting point was lower than for some of the fractions obtained from the phenylpotassium-benzene preparation but that fact is understandable because of the numerous variations from isomers and secondary changes. Attempts to separate crystalline carboxylic acids from this material proved as difficult as with the material prepared from phenylpotassium-benzene.

Phenylsodium with benzene. A preparation of phenylsodium made from amyl chloride (61 ml., 0.5 mole) and sodium (23 g., 1 atom) in benzene which had stood for 24 months showed a strong absorption at 1205 cm.$^{-1}$ and only very weak absorption in the region of 1165 cm.$^{-1}$

Phenylpotassium and anisole. A suspension of 50 ml. (28 milliequiv.) of phenylpotassium (from amyl chloride, benzene, and potassium) in heptane was allowed to react with 27 g. (0.25 mole) of anisole at room temperature for one week. Carbonation and separation of the carboxylic acid gave 2.7 g. (60%) of a beautifully crystalline (from heptane) material which melted at 102–103°, did not depress the melting point of an authentic sample of *o*-anisic acid, and showed infrared absorption identical with that sample.

A sample of *o*-potassioanisole prepared as described above was heated at 75° for 20 hr. Carbonation yielded 26 g. of phenol which was identified by the melting point of the tribromo derivative (89–92°). The large residue of tarry product which accompanied the phenol suggested that this arylpotassium compound might have undergone some change comparable to that written for phenylpotassium in Equations 2 or 3.

Butadiene and potassium reagents. Phillips research grade of butadiene (30 ml.) was polymerized in 200 ml. of pentane by 10 ml. of (a) a suspension of phenylpotassium made from either amyl chloride, benzene, and potassium or from anisole and potassium or (b) a suspension of phenylpotassium in benzene which had aged and therefore had changed to the biphenyl type product. In each case polymerization was allowed to take place for 1 hr. Then the mixture was decomposed with methanol and the solvent and excess butadiene removed by evaporation at reduced pressure. The infrared absorptions in carbon disulfide solution showed ratios of trans 1,4- to 1,2-structures (absorption at 10.34 and 10.98 microns, respectively) of 0.71.

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CAMBRIDGE 39, MASS.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MISSOURI]

A Study of the Preparation of Ketones from Mixed Aldoketene Dimers

NORMAN RABJOHN AND H. M. MOLOTSKY[1]

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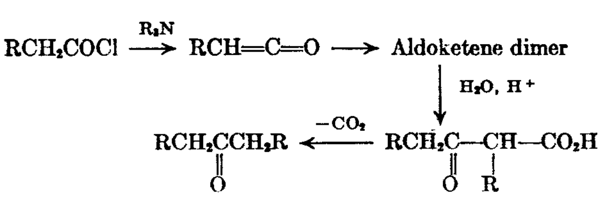
Several pairs of acid chlorides have been dehydrohalogenated by means of triethylamine, under differing conditions, to mixtures of ketene dimers. The latter have been hydrolyzed in poor yields to mixtures of symmetrical and unsymmetrical ketones. In addition, considerable amounts of acids have been obtained in most cases, which suggests that variations exist in the rates of formation and dimerization of the aldoketenes.

Sauer[2] has shown that the procedure which involves the dehydrochlorination of acid chlorides by tertiary amines to ketene dimers, followed by hydrolysis of the latter, affords symmetrical ketones in high yields. The dehydrohalogenation of a mixture of two acid chlorides would be expected to lead to four ketene dimers. Sauer[2] has demonstrated in the case of acetyl and lauroyl chlorides the formation of the two simple dimers, and one of the



$$\mathrm{RCH_2COCl} \xrightarrow{\mathrm{R_3N}} \mathrm{RCH{=}C{=}O} \longrightarrow \text{Aldoketene dimer} \xrightarrow{\mathrm{H_2O,\ H^+}} \mathrm{RCH_2\underset{\displaystyle O}{\overset{}{\underset{\|}{C}}}{-}\underset{\displaystyle R}{\underset{|}{CH}}{-}CO_2H} \xrightarrow{-\mathrm{CO_2}} \mathrm{RCH_2\underset{\displaystyle O}{\underset{\|}{C}}CH_2R}$$

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(1) Abstracted in part from the Ph. D. thesis of H. M. Molotsky, 1953.

(2) J. C. Sauer, *J. Am. Chem. Soc.*, 69, 2444 (1947).

mixed dimers, by reaction with aniline to give the corresponding acetoacetanilides. He obtained similar results with a mixture of propionyl and caproyl chlorides.

Roberts and co-workers[3] have studied the mixed aldoketene dimer of methyl and hexylketenes by the isotopic tracer technique, and have shown that it does not possess a 1,3-cyclobutanedione structure. They suggested that aldoketene dimers are best formulated probably as vinylaceto-β-lactone or β-crotonolactone derivatives.

In spite of the fact that the hydrolysis of a mixture of ketene dimers from two acid chlorides obviously will produce several ketones, it was thought that, by the proper choice conditions, one might be able to exploit the method to obtain unsymmetrical ketones in satisfactory yields. The present report describes an investigation in which several pairs of acid chlorides were dehydrochlorinated under varying conditions to mixtures of aldoketene dimers. The latter were subjected to acid hydrolysis to give mixtures of symmetrical and unsymmetrical ketones, as well as considerable amounts of other materials.

A number of preliminary experiments was carried out with acetyl chloride as the invariant reactant. The dehydrohalogenations were effected by means of triethylamine in ether solution in the usual manner.[2] After removing the triethylamine hydrochloride by filtration, the ethereal solutions were heated to reflux with dilute sulfuric acid for several hours. Although the methods employed were relatively crude, the unsymmetrical ketones were isolated in yields of 8–26% as shown in Table I. In addition to the ketonic products, dehydroacetic acid was obtained in fairly respectable yields, as well as the fatty acids corresponding to the alkyl acid chlorides employed.

TABLE I

PRELIMINARY DEHYDROHALOGENATION REACTIONS OF MIXTURES OF ACETYL AND OTHER ACID CHLORIDES

Acid Chloride	Symmetrical Ketone	% Yield[a]	Unsymmetrical Ketone	% Yield
n-Butyryl	4-Heptanone	18	2-Pentanone	13
Isovaleryl	2,6-Dimethyl-4-heptanone	12	4-Methyl-2-pentanone	8
Caprylyl			2-Nonanone	16
Undecylenyl			11-Dodecene-2-one	8
Capryl	10-Nonadecanone	13	2-Hendecanone	26

[a] Yields based upon longer chain acid chloride.

These results suggested that a more detailed investigation of the conditions for the dehydrohalogenation reaction of a mixture of two acid chlorides might lead to improved yields of the desired unsymmetrical ketones. The combination of acetyl and capryl chlorides was chosen for study, and this system was caused to react under the different experimental conditions summarized in Table II.

TABLE II

HYDROLYSIS PRODUCTS OF MIXED KETENE DIMERS FROM ACETYL AND CAPRYL CHLORIDES

	Ketones, % Yield[a]		Acidic Products, % Yield	
Conditions	2-Hendecanone	10-Nonadecanone	Capric acid	Dehydroacetic Acid
Standard procedure[b]	33	18	16	9
Ratio of acid chlorides[c] 1.4:1	13	9	17	
Ratio of acid chlorides 3:1	15	12	18	
Ratio of acid chlorides 9:1	28	17	25	17
Amine added to mixture of acid chlorides	17	18	17	
Temp. −60° for 11 hr.; 5° for 6 hr.; 25° for 24 hr.	19	20	19	15
Capryl chloride added to amine, then acetyl chloride introduced within 1 hr.	13	37	30	11
Ether replaced by toluene for solvent	18	38	29	28
Petroleum ether (b.p. 86–100°) used as solvent	10	15	19	
Carbon tetrachloride used as solvent	26	22	51	2
Acetone used as solvent	16	16	37	6
Modified standard procedure	19	12		

[a] Yields of ketones based upon longer chain acid chloride with corrections made for materials converted to corresponding acids. [b] Described in Experimental part and used in all runs with changes indicated. [c] Ratio of shorter to longer chain acid chloride.

The same basic method was followed in each of these experiments, with the exceptions indicated. The standard procedure consisted of adding an ether solution of the mixture of acid chlorides slowly to an ether solution of triethylamine which was cooled to −10 to −15°. The reaction mixture was stirred at this temperature for 9 hours, and for an additional 12 hours at room temperature. It was stirred then with 3% sulfuric acid solution to remove the triethylamine hydrochloride. The ether solution of reaction products was concentrated, and the residue was hydrolyzed with 4% sulfuric acid at 60–65° for 5 hours. The organic layer was washed with 15% sodium bicarbonate solution, dried, and fractionated. The aqueous layer was neutralized with sodium bicarbonate, extracted with ether, reacidified and again extracted with ether. Dehydroacetic acid was obtained upon concentrating the latter solution.

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(3) J. D. Roberts, Rose Armstrong, R. F. Trimble, Jr., and Marion Burg, *J. Am. Chem. Soc.*, 71, 843 (1949).

In the first four experiments listed in Table II, the ratio of acetyl chloride to capryl chloride was varied from 1.4:1 to 9:1. The results indicated that the ratio of 6:1 was the most desirable of those tried. Accordingly, this proportion was held constant during the remainder of the experiments.

The next run was designed to test the possible effects of adding the triethylamine to an ether solution of the acid chlorides. In agreement with Sauer,[2] no noticeable differences in amounts of products were observed. This may be accounted for on the basis that the tertiary amine-acid chloride complexes undergo a relatively slow rate of decomposition.

The latter factor probably was responsible also for the results obtained in the attempt to carry out the dehydrohalogenation of the mixture of acid chlorides at temperatures of 60–70° below those normally employed. It appeared that the dehydrohalogenation reaction did not occur to any appreciable extent until the reaction mixture was allowed to warm to approximately 0°.

It was thought that a variation in time of addition of the acid chlorides might have an influence on the formation of the ketene dimers. Accordingly, capryl chloride was added to an ether solution of triethylamine, and one hour was allowed to elapse before the acetyl chloride was introduced. The data from this experiment suggest that the formation of the mixed ketene dimers might have been suppressed to some extent, due perhaps to the formation of a certain amount of octylketene dimer before any ketene was present in the reaction system. It is conceivable also that the octylketene was formed fairly rapidly, but that ketene undergoes self-condensation at a rate faster than that at which it reacts with substituted ketenes.

Rice and Greenberg[4] have shown that, in general, the rate of dimerization of ketene at 0° is slower in solvents of low dielectric constant. Also, Hueter[5] has claimed that decylketene and tetradecylketene are formed from the acid chlorides of lauric and palmitic acids respectively, when they are dehydrohalogenated in carbon disulfide and benzene. Accordingly, four experiments were carried out in which the solvents were changed in the hope that it would be possible to influence favorably the rate of condensation of ketene with octylketene.

The solvents chosen for study were toluene, petroleum ether (b. p. 86–100°), carbon tetrachloride, and acetone. As shown in Table II, the yields of ketonic compounds were greatest, although perhaps not significantly so, in the case of toluene, while little or no improvements were realized with the other solvents. The results with petroleum ether were inconclusive since the overall yield of products isolated was low due to the formation of a large quantity of polymeric material.

After all but the last two experiments had been completed, it was found that the sodium bicarbonate wash had not removed all of the capric acid from the neutral fractions. This discrepancy was rectified by determining the amount of capric acid in each sample of ketone by titration with standard alkali. The neutral fractions then were washed with 15% sodium hydroxide and redistilled. In all further experiments, the mixtures from the hydrolysis reaction were extracted with sodium bicarbonate and sodium hydroxide solutions. As indicated in Table II, this is referred to as a modified standard procedure.

The dehydrohalogenations which were carried out in toluene, carbon tetrachloride, and acetone differed noticeably from the others in the larger amounts of acidic materials which were obtained. Since triethylamine hydrochloride was isolated almost quantitatively from a number of the reaction mixtures, it is conceivable that the capric acid which was recovered arose from the hydrolysis of octylketene. If this is true, then it appears that the rate of dimerization of aldoketenes is related to the nature of the solvent in which they are prepared.

Further studies were conducted then on the dehydrochlorination of the mixtures of acid chlorides shown in Table III. The following conditions were common to all of the reaction systems: ether was employed as the solvent, the ratio of the smaller to the larger acid chloride was 6:1, the ether solutions of the acid chlorides were added to an ether solution of triethylamine and the reaction mixtures were hydrolyzed by means of a 5% sulfuric acid solution at 50–65°.

TABLE III

HYDROLYSIS PRODUCTS OF MIXTURES OF KETENE DIMERS

Acid Chlorides[a]	Ketones	% Yield[b]	Acidic Products	% Yield
Acetyl and caproyl	2-Heptanone	14	Caproic acid	23
	6-Hendecanone	23	Dehydroacetic acid	10
Acetyl and stearyl	2-Nonadecanone	14	Stearic acid	23
	18-Pentatriacontanone		Dehydroacetic acid	10
Propionyl and caproyl	3-Octanone	13	Caproic acid	32
	6-Hendecanone	26	Propionic acid	8
Propionyl and capryl	3-Dodecanone	17	Capric acid	20
	10-Nonadecanone	24	Propionic acid	12

[a] Modified standard procedure used in all experiments.
[b] Yields of ketones based upon the longer chain acid chloride, with correction made for materials, converted to corresponding acids.

The results of these experiments were fairly uniform in regard to the yields of products obtained. The percentages of recovered fatty acids

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(4) F. O. Rice and J. Greenberg, *J. Am. Chem. Soc.*, **56**, 2132 (1934).

(5) R. Hueter, U. S. Patent 2,383,863 (1945); *Chem. Abstr.*, **40**, 351 (1946).

or related materials were almost as great as those of the carbonyl components. In all cases, residues were encountered which, on a weight basis, were equal to or greater than the ketonic fractions.

The data obtained from the present investigation indicate that the reaction sequence which involves the dehydrochlorination of mixtures of two acid chlorides, followed by hydrolysis of the resulting mixture of aldoketene dimers, offers little or no value as a synthetic procedure for obtaining unsymmetrical ketones. The reaction mixtures appear to be quite complex, and on the basis of the products isolated it seems that not only are the aldoketenes formed at varying rates, but that they also undergo dimerization at differing rates. The proportions of the symmetrical to unsymmetrical ketones which were obtained indicate that the formation of the mixed aldoketene dimers was not influenced greatly by the use of a considerable excess of one of the acid chlorides, or by varying a number of other factors.

The relatively large amounts of fatty acids found in most of the reaction products apparently arose from the hydrolysis of simple aldoketenes and not from unreacted acid chlorides. This result appeared to be most pronounced when carbon tetrachloride was used as a solvent. If the latter observations are correct, they indicate that the dimerization of aldoketenes is dependent to a considerable extent upon structure and reaction medium.

The results of this qualitative investigation suggest further that an extensive study of the rates of formation and dimerization of aldoketenes would be required before effective control might be exerted over the products which result from the dehydrohalogenation of a mixture of two acid chlorides.

EXPERIMENTAL

Materials. Acetyl, propionyl, *n*-butyryl, and isovaleryl chlorides were purchased from commercial sources. The other acyl chlorides were prepared from the corresponding acids and thionyl chloride. The triethylamine was purified by drying over potassium hydroxide pellets for 48 hr., refluxing with sodium until a fresh portion retained its luster, and then distilling into a receiver which contained sodium.

General aspects of the dehydrohalogenation procedures. The preliminary studies were carried out in most cases on a 1–3 mole scale. The majority of the dehydrohalogenation reactions described in Tables II and III were run on about 3.5 moles of acid chlorides. The ratio of solvent to reactants, which was not considered to be critical, was in the range of 350–400 ml. per mole of triethylamine. In all reactions, the latter was used in an excess of about 6–10%. All of the products of the reactions listed in the tables are known compounds. They were identified by comparison of their physical properties and derivatives, in many cases, with those reported in the literature.

The following procedure is representative, except for the scale of operation, of the last three experiments in Table II and all in Table III. It differs from the procedure employed for the first nine dehydrohalogenations described in Table II only in that the final hydrolysis products were washed with 15% sodium hydroxide solution as well as with 10% sodium bicarbonate solution.

Dehydrochlorination of a mixture of acetyl and caproyl chlorides and hydrolysis of the reaction product. A solution of 759 g. (7.5 moles) of triethylamine in 1000 ml. of anhydrous ether was cooled to −10° to −5° while a solution of 475 g. (6 moles) of acetyl chloride and 134 g. (1 mole) of caproyl chloride in 500 ml. of dry ether was added slowly with stirring over a period of 4 hr. The reaction mixture was allowed to remain in the ice bath for 10 hr., and then at room temperature for 24 hr. A sample of the reaction mixture gave a negative test for acid chlorides. The reaction mixture was extracted with 2000 ml. of 5% sulfuric acid solution to remove the amine salt. In some cases the latter was separated by filtration and the yields of dry triethylamine hydrochloride were approximately quantitative. The wet ether layer was separated and added to 500 ml. of 5% sulfuric acid. The ether was removed by distillation and the residue was heated at 50–65° with stirring for 4 hr. The oily layer was separated and washed with 10% sodium bicarbonate solution. The aqueous fraction was neutralized with a saturated sodium bicarbonate solution and extracted with ether. The oily fraction was mixed with the ether layer and the combined solution was extracted with a 15% sodium hydroxide solution, washed with water, and dried over anhydrous magnesium sulfate. The ether was removed in a steam bath and the residue was distilled under reduced pressure.

Two main fractions were obtained and identified as 2-heptanone and 6-hendecanone. The former, 12.5 g., boiled at 148–151°, n_D^{20} 1.4098, lit.,[6] b.p. 151°, n_D^{15} 1.41086. A semicarbazone was prepared; m.p., 122–123°; lit.,[7] m.p. 123°. The 6-hendecanone, 15.1 g., boiled at 88–90°/5 mm., n_D^{20} 1.4291; lit.,[8] b.p. 228°, n_D^{20} 1.42875.

The sodium bicarbonate soluble fraction was acidified to Congo Red with 15% hydrochloric acid solution and extracted with ether. The latter was removed by distillation and from the residue there was obtained 25.5 g. of dehydroacetic acid; m.p. 110–111°.

The sodium hydroxide soluble fraction was acidified to Congo Red with 15% hydrochloric acid solution and extracted with ether. From this solution there was obtained 25.5 g. of caproic acid; b.p., 107–110°/20 mm., n_D^{20} 1.4169, neut. equiv. 116; lit.,[9] b.p. 111.8°/20 mm., n_D^{20} 1.4163, neut. equiv. 116.

COLUMBIA, MO.

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(6) P. Ceuterick, *Bull. soc. chim. Belg.*, **45**, 545 (1936).

(7) M. L. Sherrill, *J. Am. Chem. Soc.*, **52**, 1982 (1930).

(8) I. Simon, *Bull. soc. chim. Belg.*, **38**, 57 (1929).

(9) M. Hommelen, *Bull. soc. chim. Belg.*, **42**, 243 (1933).