[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF MCGILL UNIVERSITY AND THE JOHNS HOPKINS UNIVERSITY]

Cyclobutanediones and the Lower Alkylketene Dimers[1,2]

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The Schroeter synthesis of the 2,4-dimethyl and the 2,4-diethyl derivatives of 1,3-cyclobutanedione has been repeated and the products have been studied intensively. Fairly close agreement in physical properties between our methyl derivative and that of Schroeter was noted, but our ethyl derivative demonstrated an elevated melting point, and, in comparison with the methyl analog, such great instability as to cast doubt upon its proposed cyclobutane structure. Ethereal solutions of the lower alkylketenes were prepared by the Staudinger process, and it was shown by direct comparison that both methyl- and ethylketenes, but not isopropylketene, dimerize to give cyclobutane products. The lactone dimers obtained by the Wedekind dehydrohalogenation of acyl halides were shown to be absent under the conditions of our experiments, except for isopropylketene. Finally, some evidence is advanced to show that the solid cyclobutane dimers are terminal rearrangement products of liquid polymers of as yet unknown constitution.

In the course of his work on alkylketenes Staudinger[4] obtained a solid compound, presumed to be a dimer, from an ethereal solution of methylketene that was allowed to stand. Since the substance was enolic it was assigned the cyclobutene structure II (Fig. 1). The only evidence substantiating the proposed structure is the abbreviated statement by Schroeter[5] that there was no depression on taking the mixed melting point of the ketene polymer with a compound which he had shown *via* circumstantial evidence[5,6] to be the cyclobutanedione I. In reinvestigations[7,1] of this synthesis it has been shown conclusively that dimethylcyclobutanedione (I)[7] is formed, albeit through the very unusual intermediate 3,5-dimethyl-2-hydroxy-6-ethoxy-γ-pyrone (IV), rather than the postulated[5,6] cyclobutane ester V.

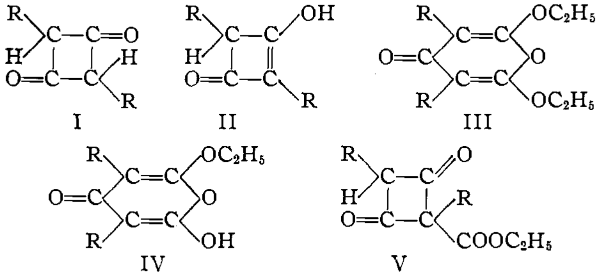

Fig. 1.

In our work with the Schroeter synthesis[5] it was noted that the pyrone IV (R, methyl), and the 2,4-dimethyl-1,3-cyclobutanedione (I) derived from it, not only melted somewhat higher than the reported values,[5] but in addition I demonstrated a stability much beyond that indicated by the original author.[5] On the other hand, the ethyl analogs, though melting much higher than reported, were much less stable than the methyl derivatives. After we had established, *via* elaborate purifications,[8] that this behavior was not due to impurities, a critical examination was then made of the condensation product of ethyl α,α'-diethylacetonedicarboxylate in an effort to uncover evidence at variance with either the pyrone or the cyclobutanedionecarboxylic ester structures (IV or V). This was not, at first, successful; hydrolysis with boiling water furnished carbon dioxide and ethyl α-butyrylbutyrate[9]; alcoholic potash at room temperature was without action[1]; the Zeisel determination revealed one ethoxy group; and although the Kurt-Meyer enol titration was negative, methylmagnesium iodide indicated the presence of one active hydrogen with additional Grignard carbonyl reaction to the extent of 80%. We repeated the carbethoxylation[5] of the condensation product with ethyl chloroformate, obtaining presumably the 2-carbethoxy pyrone derived from IV, a substance of considerably lower boiling point than that reported by the German author. We do not at this time regard this difference as being of great significance,[10] since our product duplicated the behavior of Schroeter's in regenerating the original condensation product under the catalytic influence of sodium ethoxide.

Chemical proof was finally secured for the pyrone structure (IV) of the acidic condensation product through treatment with diazoethane. The basic pyrone III (R, ethyl) was obtained; III was also isolated as the acid-soluble, base-insoluble fraction from the sulfuric acid condensation of ethyl α,α'-diethylacetonedicarboxylate when carried out in the known manner.[7,1,6] No doubt attaches to the structure of III,[11] and its identity with the ethylation product would seem to eliminate definitely the cyclobutanedionecarboxylic ester from consideration (compare 7 and 1). Physical evidence substantiating the chemical proof was obtained from the infrared absorption spectra[12] of the two related pyrones, *viz.*, 3,5-dimethyl-2-hydroxy-6-ethoxy-γ-pyrone and 3,5-diethyl-6-ethoxy-2,4-pyronone. While the curves are similar, certain important differences appear. In the

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[1] For the first paper in this series see E. B. Reid, THIS JOURNAL, **72**, 2853 (1950).

[2] Most of the material in this paper was presented before the Organic Division of the Buffalo Meeting of the American Chemical Society, March 24, 1952.

[3] Part of this paper is taken from the doctoral dissertation of Stephen J. Groszos, The Johns Hopkins University, Baltimore, Md., 1951.

[4] H. Staudinger, *Ber.*, **44**, 533 (1911).

[5] G. Schroeter, *ibid.*, **49**, 2697 (1916); compare J. D. Roberts, R. Armstrong, R. F. Trimble, Jr., and M. Burg, THIS JOURNAL, **71**, 843 (1949), footnote 8.

[6] G. Schroeter and C. Stassen, *Ber.*, **40**, 1604 (1907).

[7] R. B. Woodward and G. Small, Jr., THIS JOURNAL, **72**, 1297 (1950).

[8] These are described in the experimental part.

[9] G. Schroeter, ref. 5, had shown that hydrolysis of the methyl analog gave carbon dioxide and ethyl α-propionylpropionate.

[10] The possibility exists, and is under investigation, that the acidic sulfuric acid condensation products obtained by Schroeter, *et al.*,[5,6] were in fact the cyclobutanecarboxylic esters (V) as originally formulated, and not the isomeric pyrones (IV) that have been obtained by Woodward and Small,[7] and by Reid,[1] and in the present work.

[11] G. Schroeter, *Ber.*, **59**, 973 (1926).

[12] Our thanks are due Dr. Lester P. Kuhn of the Ballistic Laboratory, Aberdeen Proving Grounds, and Mrs. Marjorie H. Melville of The Johns Hopkins University, for their assistance in these determinations.

case of the ethyl pyrone no OH absorption is observed at about 3 μ (3400 cm.$^{-1}$), in contrast with the wide band shown in this region by the acidic methyl pyrone. Of interest also is the strong carbonyl absorption for both pyrones, occurring at 5.8–6.0 μ (1700 cm.$^{-1}$), excluding the possibilities of either conjugated chelated structures or externally hydrogen-bonded OH.[13] The ethylpyrone is thus the non-enolic analog of the methyl derivative described earlier.[1]

Turning now to the question of the diethylcyclobutanedione, I, we found that our ethylpyrone underwent saponification and decarboxylation with hot baryta to yield a crystalline strongly acidic enol that was empirically identical with Schroeter's product, although its melting point was much higher. Again, various tests were carried out to establish either the identity or non-identity of our substance with his. These did not, however, yield decisive information. Thus, hydrolysis readily cleaved the molecule to yield carbon dioxide and di-*n*-propyl ketone (compare the dimethylcyclobutanedione, I).[5] Although the properties of derivatives seemed to indicate complete similarity between the two, our compound failed to form either a mono- or a dioxime, and in addition proved inert to hydrogen in the presence of Adams catalyst. Further, attempted ozonization merely caused rapid decomposition of the compound, apparently to the same oily product formed on keeping the solid under ordinary conditions for about ten days. In the Grignard machine a specimen behaved abnormally, showing 1.3 active hydrogens with 1.7 additions to carbonyl groups.[14]

Since it appeared impossible either to duplicate Schroeter's synthesis of 2,4-diethyl-1,3-cyclobutanedione or to prove by degradations the cyclobutane structure of our product, our attention turned to the preparation of the dimers of methyl- and ethylketene, for such would make possible direct comparisons of (a) the dimer of methylketene with the known[7] 2,4-dimethyl-1,3-cyclobutanedione, and (b) the dimer of ethylketene with our high-melting derivative. An apparatus was designed (see Experimental part) that successfully overcame experimental difficulties,[15] and furnished ethereal solutions of methyl-, ethyl- and isopropylketenes.[16] From methyl- and ethylketene solutions by appropriate treatment were obtained both solid and liquid polymers; isopropylketene solutions failed to furnish solid material.

Solid Methylketene Dimer.—The solid product was obtained from solutions that had been allowed to stand. It was obtained in the form of a microcrystalline powder, and attempts to crystallize it in the form of long needles identical with those formed by I were without success. Nevertheless molecular weight determinations showed the substance to be a dimer of methylketene, and direct comparisons *via* physical and chemical tests proved that the substance possessed structure I. Not only were the infrared absorption spectra[12] of both specimens virtually superposable, but the typical bands ascribed to the OH frequency[13] of either associated or non-associated hydroxyl groups were absent. The substance thus appears to be diketonic in the solid state and this was further indicated by the position and sharpness of the carbonyl band at 5.8 μ. The spectra also show a maximum at 10.9 μ, which is of interest in connection with the cyclobutane structure of the substance since it has been reported recently[17] that cyclobutane hydrocarbons exhibit a characteristic absorption at 10.9–11.0 μ, ascribed to the methylene rocking frequency. Likewise the infrared spectra of the dioximes of the two specimens were identical, and gave a doublet at 10.6 and 10.9 μ, probably due to ring stretching and methylene rocking respectively.[18] The X-ray diffraction patterns of both specimens were obtained by the powder method, and since the lines may be superposed one upon the other, it follows that the two samples are composed of the same substance and are not dimorphic modifications,[19] despite our inability to obtain them in identical crystalline form.

Although I appears to be diketonic in the solid state, in solution it is substantially ionic. This was made apparent from a study of the effects of concentration and solvent upon the ultraviolet absorption spectra of the compound.[20] In ethanol, using concentrations of 4, 10, 20 and 200 $\times 10^{-5}$ M, a set of intersecting curves was obtained, giving the isosbestic point[21] at λ 244 mμ, log ϵ 4.01. The non-applicability of Beer's law, shown by the shift of maxima to longer wave lengths with decreasing concentration, and the isosbestic point clearly show the presence of an equilibrium between two species, each of which obeys Beer's law. Changing from ethanolic to aqueous solution also caused a shift of maxima toward longer wave lengths, but the further change from water to dilute sodium hydroxide occasioned very little shift of the maxima. This, together, with the fact that only a slight displacement toward shorter wave length occurred on going from ethanol to dilute hydrochloric acid indicates that the enol is mainly ionic in hydroxylic solvents.

Solid Ethylketene Dimer.—As was found with the solid methylketene dimer, analysis, mixed melting points, infrared and ultraviolet absorption spectra, and X-ray diffraction patterns clearly showed the solid ethylketene product to be identical with 2,4-diethyl-1,3-cyclobutanedione as pre-

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(13) Compare R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, This Journal, **71**, 1068 (1949); also E. B. Reid and W. R. Ruby, *ibid.*, **73**, 1054 (1951).

(14) Dimedone also behaves abnormally. See ref. 7.

(15) C. D. Hurd, F. W. Cashion and P. Perletz, *J. Org. Chem.*, **8**, 367 (1943), report unsuccessful attempts to obtain ketene or methylketene by the Staudinger method.

(16) Isopropylketene has not heretofore been prepared. H. Staudinger and H. W. Klever, *Ber.*, **41**, 906 (1908), report the preparation of an ethereal solution of ethylketene but no polymeric products could be obtained from it.

(17) J. M. Derfer, E. E. Pickett and C. E. Boord, This Journal, **71**, 2482 (1949).

(18) Compare T. P. Wilson, *J. Chem. Phys.*, **11**, 369 (1943).

(19) Compare E. L. Jackson, This Journal, **72**, 395 (1950), who obtained widely different X-ray patterns for the dimorphic forms of a substituted sulfone.

(20) We wish to thank Dr. R. C. Hirt, Research Laboratories, American Cyanamid Co., Stamford, Conn., for measuring the spectra in acid and base.

(21) W. West, "Spectroscopy and Spectrophotometry," Physical Methods of Organic Chemistry II, First Edition, edited by A. Weissberger, Interscience Publishers, Inc., New York, N. Y., 1946, p. 775.

pared by us according to the Schroeter procedure.[1] In general the ultraviolet absorption spectra of the diethylcyclobutanedione in ethanol duplicated the behavior of the methyl analog in its failure to obey Beer's law, and in the position of its isosbestic point at λ 242 mμ, log ϵ 3.95. From the potentiometric titration of the ethyl derivative its K_a was calculated to be 3.2×10^{-4}, and its pK_a to be 3.5. Comparison with the data of Woodward and Small[7] for 2,4-dimethyl-1,3-cyclobutanedione shows that the latter is a fivefold stronger acid. Comparison of the infrared absorption curves of the methyl and ethyl derivatives of I shows that the absorption at 10.9 μ, characteristic for hydrocarbon-substituted cyclobutanes[17] and for the methyl derivative, is lacking for the ethyl analog. There is for the latter, however, a maximum at 11.3 μ and it seems entirely likely that substitution of ethyl groups for methyl on the cyclobutanedione ring causes this shift toward longer wave lengths of the ring methylene vibrations, possibly through steric interaction with the carbonyl groups.[22]

Liquid Polymers.—Only with isopropylketene was *the non-enolic lactone* type of dimer[23,24] obtained. While oily by-products accompanied the *spontaneous* formation of solid cyclobutanediones from methyl- and ethylketene, these were of different structural type. This point was checked specifically for the methyl derivative by the preparation of the "Wedekind" lactone dimer of methylketene *via* dehydrohalogenation of propionyl chloride.[24] The physical properties of this compound, including its infrared absorption spectrum,[25] were completely different. Moreover, from the published data concerning the "Wedekind" dimer of ethylketene,[26] it is clear that this substance was not produced under our experimental conditions. Isopropylketene thus presented an interesting anomaly, in that instead of crystalline material, a colorless, lachrymatory, non-enolic oil was formed. Treatment of this with aniline gave a product, $C_{16}H_{28}O_2N$, apparently identical (except for a low melting point) with the anilide prepared by Sauer from the liquid lactone isopropylketene dimer.[24]

On the other hand, the amounts and natures of the liquid by-products obtained from both methyl- and ethylketene varied according to the immediate history of the ethereal solutions. Thus, one specimen of ethereal methylketene was allowed to stand at room temperature for four days before being concentrated to a yellow enolic oil. This oil, on distillation *in vacuo*, yielded a single fraction which rapidly turned red, and then purple. As solid 2,4-dimethyl-1,3-cyclobutanedione was being deposited, the color changed back to red and finally to pink. After standing at 5° for one week, all of the liquid had changed to a mass of pink crystals. This transformation of liquid polymer (of unknown constitution) to the solid dimer was quantitative. Under other conditions the polymerization reaction took a different course. For example, after standing at room temperature for 29 days an ethereal solution of methylketene furnished solid dimer along with oil. Distillation of this oil gave diethyl ketone, along with three high-boiling fractions, each of which, on long standing, deposited some solid dimer. The residual oil was strongly enolic, and failed to give ketonic derivatives. Nevertheless, examination of the infrared absorption spectrum of this residual oil shows a very strong carbonyl absorption at 5.8 μ, and the width of this band indicates a conjugation involving hydroxyl and carbonyl groups. Because of the strongly enolic nature of the oil, a β-diketone or β-keto ester type of structure is possible. Of significance is the fact that, contrary to Staudinger,[27] the action of base upon the liquid polymer did not produce solid dimer.

In a further study, an ethereal methylketene solution was allowed to stand, exposed to *dry air*, for seven months at room temperature. Besides some solid cyclobutanedione, this specimen yielded a pungent non-enolic oil. This oil appeared to be an oxidation product, presumably resulting from the action of atmospheric oxygen upon the ketene or its polymer (the solvent ether may also have been involved), for an attempted distillation of the oil at atmospheric pressure resulted in a violent explosion. Beyond this, efforts to identify the substance were without success. It is of interest in this connection that only the autoxidation of dialkylketenes has been recorded,[28] alkylketenes were presumed to polymerize too quickly for autoxidation to occur, to form non-autoxidizable cyclobutanediones.

Work in the ethyl series was somewhat complicated by the presence of halide in the ketene distillate, and by the instability of the solid dimer. The latter may be responsible for the fact that, despite considerable experimentation, we were unable to establish conditions under which the transformation of distilled liquid polymer to 2,4-diethyl-1,3-cyclobutanedione would take place. Indeed, our best results were obtained by allowing the ethereal solution to stand at refrigerator temperature, exposed to dry air, for six days. Concentration of the solution gave the solid dimer of m.p. 87–88° (dec.) along with a green yellow oil. Distillation of this oil, *in vacuo*, furnished some di-*n*-propyl ketone along with what appeared to be an oxidation product (whose properties were similar to those obtaining for the aged methylketene solution). A third, high-boiling liquid was also obtained. This substance distilled as a light yellow enolic oil, but it rapidly became dark red. On standing at room temperature for several months the oil assumed an orange color. No solid dimer, however, could be obtained from the distilled oil. The infrared absorption spectrum was taken and is generally similar to that of the by-product oil obtained from the polymerization of methylketene. Finally, the infrared spectra of the lactone dimer of methylketene[25] and of its

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(22) Compare the effect of carboxy groups on the characteristic absorption of the cyclobutane methylene carbons, E. R. Reid and M. Sack, THIS JOURNAL, **73**, 1985 (1951).

(23) E. Wedekind and W. Weisswange, *Ber.*, **39**, 1631 (1906).

(24) J. C. Sauer, THIS JOURNAL, **69**, 2444 (1947).

(25) We wish to thank Dr. F. Halvorson of the Stamford Research Laboratories, American Cyanamid Co., for this measurement.

(26) R. L. Wear, THIS JOURNAL, **73**, 2390 (1950). See also A. S. Spriggs, C. M. Hill and C. W. Senter, *ibid.*, **74**, 1555 (1952).

(27) H. Staudinger, "Die Ketene," Ferdinand Enke, Stuttgart, 1912, p. 42; H. Staudinger, *Ber.*, **53**, 1085 (1920).

(28) H. Staudinger, "Die Ketene," F. Enke, Stuttgart, 1912, p. 49,

polymerization product were measured. No similarity was apparent between the spectra of the lactone dimer and the liquid by-products obtained from either methyl- or ethylketene.

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Experimental

Ethyl Acetonedicarboxylate.—Regeneration of the ester[29] from its potassium enolate[30] furnished a product in 46% yield (recovery), that had b.p. 135° at 11.0 mm., and n^{22}D 1.4392[31] when distilled from a 2-foot Podbielniak type column whose efficiency was 8 theoretical plates. Pure ester, of the same b.p. and n^{22}D 1.4390,[31] was also obtained by hydrolysis of the recrystallized semicarbazone,[32] effected by shaking the crystals with dil. hydrochloric acid (1:4) maintained at 0°, and separating the resultant ester layer. The yield of recovered ester was 33%.

Sulfuric Acid Condensation.—Ethyl α,α'-diethylacetonedicarboxylate was condensed according to the previously described procedure.[5,1] The acidic pyronone was purified by precipitation with dil. hydrochloric acid from its sodium carbonate solution. The yields varied from 34–53%, the products from different runs showing different melting points. According to Schroeter[5] the m.p. is 101–102°. The highest m.p., 112–114° (slight dec.), was obtained after a specimen was recrystallized several times from aqueous ethanol. A typical specimen had m.p. 107–108° after recrystallizations from aqueous ethanol and ethyl acetate.

Anal. Calcd. for $C_{11}H_{16}O_4$: C, 62.26; H, 7.55; ethoxyl, 21.2. Found: C, 62.16; H, 7.75; ethoxyl (determined on a different sample), 21.3; measurement in the Grignard machine showed 1.1 active hydrogen present, with 80% addition of Grignard reagent to other groups.

The most carefully purified material decomposed after ten days at room temperature, to a sour-smelling oil. Under refrigeration, however, the material was stable for more than a month.

The basic 3,5-diethyl-2,6-diethoxy-γ-pyrone was obtained from the diluted condensation medium,[11] and had m.p. 45–46° after recrystallization from petroleum pentane.

Anal. Calcd. for $C_{13}H_{20}O_4$: C, 64.97; H, 8.41. Found: C, 65.17; H, 8.55.

Tests on 3,5-Diethyl-6-ethoxy-2,4-pyronone.—The pyronone was inert to hydrogen at 40 p.s.i. in the presence of Adams catalyst, and also to alcoholic potassium hydroxide on standing for several weeks. The ferric chloride enol test required several hours for the appearance of color, and the compound showed zero enol content in the Kurt Meyer titration. *Hydrolytic Degradation:* On refluxing a mixture of recrystallized pyronone with distilled water for one hour a clear supernatant oil formed, with carbon dioxide elimination. The oil boiled mainly at 105° at 12–13 mm., and on treatment with hydrazine hydrate yielded the expected ethylpropylpyrazolone,[33] identical with that prepared from ethyl α-butyrylbutyrate of b.p. 106–107° at 13.0 mm.[32] *Alkoxylation:* When carried out according to the reported directions[5] our high-melting pyronone formed an oil, b.p. 142–143° at 1.0 mm. The reported b.p. is 162–163° "im Hochvacuum." Despite this difference in b.p. our product underwent immediate de-alkoxylation on treatment with ethanolic sodium ethoxide, to regenerate the original high-melting pyronone. *Alkylation:* Two grams of ethanol-moistened pyronone was treated at 0° with an excess of ethereal diazoethane. The reaction was vigorous, and the product, on working up according to the previously described procedure,[1] consisted of an oil together with the basic 2,5-diethoxy-3,5-diethyl-γ-pyrone described above, m.p. and mixed m.p. 45–46°. The yield was 0.33 g., or 14.4%.

2,4-Diethyl-1,3-cyclobutanedione.—The procedure of Schroeter[5] was followed with the exception that the mixture of baryta and pyronone was stirred vigorously at 85° (inside temperature), for six hours before being worked up in the same way as the methyl analog.[1] The yield was variable, 18–45% of product that had m.p. 87–88° (slight dec.) after several recrystallizations from ethyl acetate or water, from which it was obtained as small colorless needles. Schroeter gives[5] 76–78° for the m.p. of his product. The compound could be stored at −78° for more than a month; at 20° decomposition set in after six to eight days.

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.24; H, 8.12; measurement in the Grignard machine showed 1.3 active hydrogens present with 1.7 Grignard additions to other groups.

Tests on 2,4-Diethyl-1,3-cyclobutanedione.—With phenylhydrazine the derivative[5] m.p. 131–133°, was readily obtained. However, the compound failed to react with hydroxylamine reagent, and proved inert to hydrogen at 35 p.s.i. with Adams catalyst for 24 hours. In an attempted ozonization in carbon tetrachloride solution the compound absorbed ozone but apparently gave the same decomposition product formed by allowing it to stand exposed to air at room temperature for about six days. *Hydrolytic Degradation:* On refluxing a mixture of the dione and water for one hour, carbon dioxide was eliminated. A yellow-colored di-*n*-propyl ketone formed. The latter was confirmed by the semicarbazone.

Preparation of Allylketenes and Polymers.—The apparatus given in Fig. 2 was devised as the result of many comparative experiments.

Operation.—All operations were conducted under a constant flow of anhydrous oxygen-free nitrogen which was prepared *in situ* by leading a stream of commercial nitrogen through the furnace (1) containing copper at 450°, and thence through the drying tube (3) which contained phosphorus pentoxide (middle zone) separated by glass wool from layers of "indicating" Drierite. The purified nitrogen then passed the flowmeter (5). For purposes of sweeping the apparatus free of oxygen and moisture, the nitrogen by-passed, by means of stop-cock 8, the trap and mercury bubbler (6); during a run it was necessary to pass the nitrogen through the trap and bubbler to prevent backflow of ether vapor from the reaction flask (12).

In making a run the bromoacyl bromide was added dropwise from the dropping funnel (10) to a rapidly stirred suspension of activated zinc dust[34] in absolute ether containing a small amount of fused zinc chloride to initiate the dehalogenation.[35] The halide was added as rapidly as possible *together* with an additional quantity of absolute ether from the dropping bottle (9). For a one-half mole run the *total* quantity of ether used was 1200 ml. During the addition of the reactants a rapid distillation was maintained by external heating. The condensing system (13, 14 and 15) consisted of a trap (capacity about 500 ml.) containing absolute ether at −60°. It was assumed that as long as no ether was lost from the trap, the ketene was retained. The efficiency of trap 14 was such that the auxiliary trap (17) was scarcely needed. The traps were cooled with baths containing methyl Cellosolve and Dry Ice. When the ether-ketene distillate had filled the trap (14), it was siphoned (under nitrogen pressure) into the storage vessel (21), the latter being kept at any temperature desired. Because of the highly toxic nature of simple ketene (and also its dimer)[36] the storage flask (21) was connected through the drying tube (19) to a good fume hood.

The reaction was variable in rate, especially during the initial stages; the consequent variations in pressure were somewhat accommodated by attachment of the 1-liter flask (4) which materially increased the volume of the system. Comparative studies showed it was necessary to distil the ether–ketene mixtures away from the inorganic residues as fast as possible, presumably due to polymerization induced by the zinc bromide. For this purpose, the neck of the

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(29) R. Adams and H. M. Chiles, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 237.

(30) H. v. Pechmann, *Ann.*, **261**, 155 (1891).

(31) Measured six days after distillation to ensure keto–enol equilibrium.

(32) A. Haller and F. March, *Bull. soc. chim.*, [3] **31**, 440 (1904).

(33) L. Bouveault and R. Locquin, *Bull soc. chim.*, [3] **31**, 588 (1904).

(34) R. L. Shriner, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 16.

(35) We wish to thank Dr. Howard Haas, Research Department, Polaroid Corp., Cambridge, Mass., for suggesting this means of overcoming lengthy induction periods. See H. Haas, *J. Polymer Sci.*, **5**, 515 (1950).

(36) H. A. Wooster, C. C. Lushbaugh and C. E. Redeman, THIS JOURNAL, **68**, 2743 (1946).

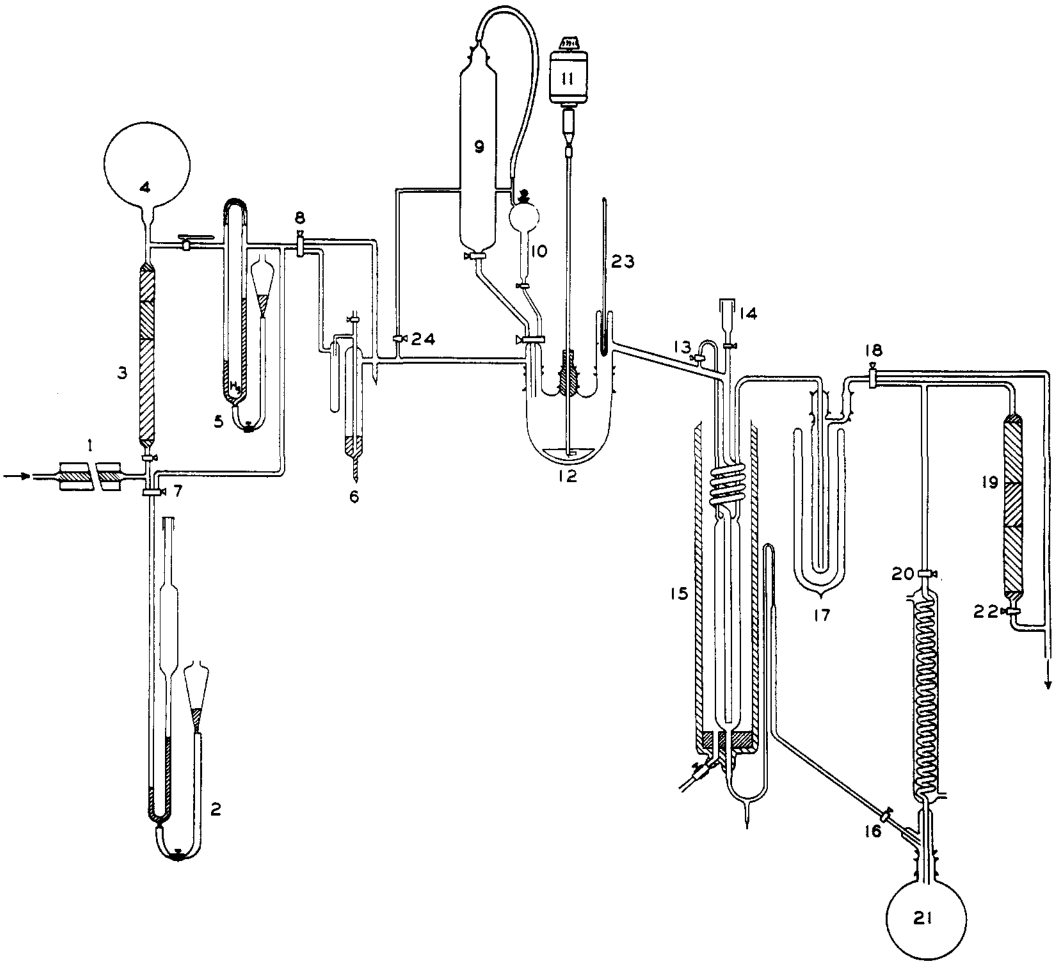

Fig. 2.—Apparatus for the preparation of alkylketenes and their dimers.

flask carrying the thermometer (23) was made as short as possible, consistent with retaining the acyl halides in the vessel. Various solvents other than ether were tried, but always to the detriment of the reaction, and some diethyl ether was needed to initiate the reaction when low-dielectric solvents such as benzene were used. Only very poor yields of products were obtained under these conditions however. In one attempt to obtain methylketene free of solvent, di-*n*-butyl ether was used as the reaction medium. This resulted in only traces of polymerized product together with unreacted halide.

Methylketene Products.—The following preparation is typical. After thorough drying of the apparatus by sweeping with dry nitrogen, 100 g. (0.46 mole) of α-bromopropionyl bromide was added to 60 g. (0.92 mole) of activated zinc dust in absolute ether containing a small amount (0.5 g.) of fused zinc chloride. The ethereal distillate[37] which is colorless at the temperature of the trap,[38] was allowed to stand at 5° for about two weeks, and the solvent then removed under aspirator pressure at 35°. The residue consisted of a pale yellow slightly lachrymatory oil mixed with colorless solid; the total yield was 13–14%, of which at least 5% was solid dimer. After filtration of the chilled residue, the solid was recrystallized from ethyl acetate and obtained in the form of a microcrystalline powder, m.p. 140–141° (slight dec.).[39] A mixed m.p. with 2,4-dimethyl-1,3-cyclobutanedione of m.p. 140–141° (slight dec.), prepared by Schroeter's method,[5,1] gave 139.5–140.5° (slight dec.). The solid ketene dimer was analyzed.

Anal. Calcd. for $C_6H_8O_2$: C, 64.27; H, 7.15. Found: C, 64.38; H, 7.10.

Both I and the dimer gave immediate intense red colors with dil. ferric chloride solution, and dissolved with effervescence in aqueous sodium carbonate. The dioximes were prepared,[5] yielding colorless needles in about 15% yield. The m.p. of the dioxime of the I was 188–189° (dec.); that of the dimer was 187–188° (dec.), and the mixed m.p. was not depressed. The m.p. of this derivative has been given by Schroeter[5] as 196–198° (dec.) and by Woodward and Small[7] as 198–200°.

Anal. of dioxime (by Mrs. J. E. Buck). Calcd. for $C_6H_{10}O_2N_2$: N, 19.71. Found for dioxime of dione: N, 19.52. Found for dioxime of polymer: N, 19.67.

Molecular Weight.—A modification[40] of the isopiestic method was employed. The solid I was considered to be the known reference compound, $C_6H_8O_2$, molecular weight 112.12, referred to below as B, and the solid from methylketene, A, was equilibrated against it. The molecular weight was calculated, using the expression

$$\text{Mol. wt. of A} = \frac{(\text{wt. of A}) \times (112.12) \times (\text{vol. soln. of B})}{(\text{vol. soln. A}) \times (\text{wt. of B})}$$

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[37] The yield of monomeric ketene was 4.9%, based on the amount of propionanilide, m.p. 104°, formed by treating the ethereal solution with aniline.

[38] If the colorless solution is allowed to warm to room temperature, a straw-yellow color develops, which fades almost completely within two hours. On standing at room temperature for two days, however, the same solution becomes light yellow. It may be noted that although the color is generated only on warming, the process is not reversed by chilling. It is also of interest that ethereal solutions of dimethylketene, which polymerize to 2,2,4,4-tetramethyl-1,3-cyclobutanedione in relatively high yield, are reported to be yellow in color (C. D. Hurd and M. F. Dull, THIS JOURNAL, **54**, 2432 (1932)).

[39] The m.p. appears to be affected profoundly by rate of heating and traces of impurities. Occasionally specimens were obtained with m.p. as high as 142–143°, and as low as 132–134°.

[40] The method used was that of G. Barger, *J. Chem. Soc.*, **85**, 286 (1904), as modified by A. H. Corwin, The Johns Hopkins University, unpublished work.

Using ethyl acetate as solvent, equilibrium was reached after 233 hours at 40°, and gave 110.5 (1.4% error) for the molecular weight of the polymer.

X-Ray Diffraction Data.—These data were obtained by the "powder method," using cobalt radiation; 35 kv., 12 milliamps. A General Electric No. 155 camera was used, and the time of exposure was four hours.

Liquid Methylketene Products.—(a) *After four days* at room temperature, the ether and solid dimer were removed, and the residual oil was distilled under nitrogen at 3.0 mm. A single fraction, b.p. 79–80°, was obtained, and a solid residue (shown to be I) remained. After only a few minutes the colorless distillate assumed a red color, and then rapidly turned an intense purple. On standing for an hour at room temperature the color changed to a bright red, and a small quantity of white crystals had separated. After two days a large amount of the oil had turned solid; the sample was then placed in the refrigerator at 5°, and kept there for one week, by which time all of the oil had become a mass of light pink crystals. The transformation was quantitative, and the solid was shown to be I.

(*b*) *After twenty-nine days* at room temperature, the ether was removed from the polymerization products, leaving a yellow oil and solid I. The oil was distilled from nitrogen at 0.08–0.10 mm. and the following fractions, besides some diethyl ketone, were collected: (b.p., $n^{26}\text{D}$) 55–91°, 1.4542; 91–99°, 1.4578; 99–101°, 1.4591. On standing at room temperature for three weeks all three fractions slowly deposited solid I. The clear supernatant oil from all three fractions now had $n^{26}\text{D}$ 1.4533, indicating the same composition. Fractions 2 and 3 were combined and used for tests. This oil was strongly enolic, and free of halogen. It failed to yield an oxime, or a derivative with *o*-phenylenediamine. It was insoluble in water, but dissolved in aqueous sodium bicarbonate with effervescence. Acidification of this, or of a sodium hydroxide solution of the liquid polymer, did not furnish the solid dimer.

Analysis of this oil, and also of a specimen isolated from another run, indicated that oxygen had reacted with the methylketene during polymerization, to yield a mixture of products not accommodated by any simple formula.

(c) *After seven months* at room temperature, during which the ethereal solution was exposed to air (through a calcium chloride drying tube), some solid I was obtained together with an oil residue. The latter was distilled at 3.5 mm., under nitrogen, to yield a colorless pungent oil, b.p. 41–46°. This material, whose general properties have been described in the text, appeared to be of peroxide nature. An attempt was made to distil the substance at atmospheric pressure; at a temperature of about 140° the distilling flask exploded violently. The substance reacted readily with 2,4-dinitrophenylhydrazine and with semicarbazide reagent to form unidentified derivatives.

Ethylketene Products.—The ethereal solution, prepared in essentially the same manner as for the methyl analog and showing the same temperature–color behavior, was allowed to stand under refrigeration protected from moisture, for about one week. The ether was removed at aspirator pressure at 25°. The residue was then cooled in a Dry Ice-bath for an hour until a magma formed. Rapid filtration through a buchner funnel, previously made very cold with Dry Ice, was necessary to prevent re-solution of the solid. The solid was then taken up in the minimum amount of absolute ethyl acetate at room temperature, filtered, and the filtrate cooled to Dry Ice temperature. The colorless solid appeared in the form of clusters of short needles when viewed under the microscope. After two recrystallizations the m.p. was 87–88° (slight dec.).

Anal. Calcd. for $C_8H_{12}O_2$: C, 68.57; H, 8.63; neut. equiv., 140.2. Found: C, 68.33; H, 8.79; neut. equiv., 139.7.

In every respect this solid polymer proved identical with the high-melting diethylcyclobutanedione.[5] The yield of crude halogen-containing magma was variable, 30–70%, but the best yields of recrystallized solid obtainable from the magma varied from 0.5–1.0%.

Liquid Ethylketene Products.—The yellow oil by-products were distilled under nitrogen yielding di-*n*-propyl ketone together with an oil, b.p. 33–35° at 0.7 mm. The latter formed with 2,4-dinitrophenylhydrazine a derivative of m.p. 158–159° (depressed on admixture with diethyl ketone 2,4-dinitrophenylhydrazone of m.p. 156°), and giving the same analysis as obtained for the corresponding derivative got from the aged methylketene solution. A third fraction, b.p. 74–100°, was obtained as a yellow oil that rapidly turned dark red. This fraction gave a strong enol test with ferric chloride solution, but no solid dimer could be obtained from it.

Isopropylketene.—A mixture of α-bromoisovaleryl bromide and chloride[41] reacted readily with zinc to yield a typical ethereal solution (colorless at −60°, pronounced yellow at room temperature). No solid polymer could be obtained regardless of the length of time the solution stood. After two days at refrigerator temperature, a portion of the solution was treated with aniline, and the product washed with water and recrystallized from aqueous alcohol. The m.p. was 94–95°; Sauer[24] gives 105–106°, for his specimen of α-isovalerylisovaleranilide.

Anal. Calcd. for $C_{16}H_{23}O_2N$: C, 73.9; H, 8.87. Found: C, 73.7; H, 8.84.

Tests on the oil left after evaporation of the ether showed that no enolic dimer was present in specimens that had stood as long as 20 days.

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(41) E. Fourneau and V. Nicolitch, *Bull. soc. chim.*, [4] **43**, 1232 (1928).