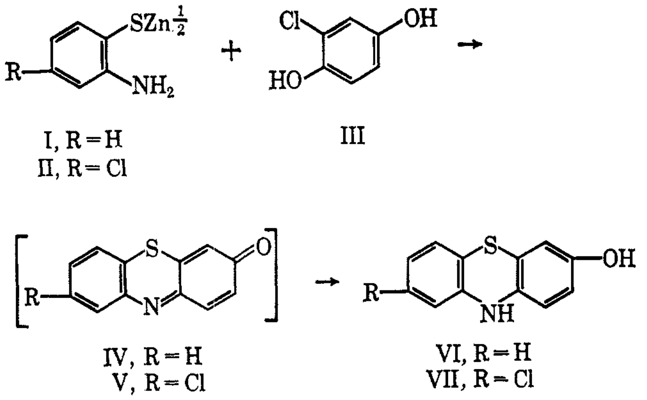
SCHEME I



method described by Steiger.[6] Reduction of commercial bis(4-chloro-2-nitrophenyl) disulfide in acetic acid with zinc dust and hydrochloric acid provided 84% of the mercaptide II.[7]

Mixtures of the zinc salts I and II and chlorohydroquinone (III) were treated, in aqueous–ethanolic sodium hydroxide, with oxygen. The reaction mixtures, which now contained the phenothiazones IV and V, were simply poured into aqueous sodium hydrosulfite. Routine purification of the resulting precipitates gave a 67% yield of 3-hydroxyphenothiazine (VI) and a 62% yield of 2-chloro-7-hydroxyphenothiazine (VII). The substitution of 3-chlorocatechols for 2-chlorohydroquinone should make accessible various 1- and 9-hydroxyphenothiazines.

Experimental Section[8]

2-Aminobenzenethiol Zinc Salt (I).—To a solution of 8 g (0.2 mole) of sodium hydroxide in 25 ml of water was added 25 g (0.2 mole) of 2-aminobenzenethiol. The volume of the mixture was increased to 250 ml with water, and the mixture was warmed to help effect solution. The solution was filtered to remove a small amount of yellow insoluble material, and the filtrate was poured into a solution of 15 g (0.11 mole) of zinc chloride in 45 ml of glacial acetic acid and 250 ml of water. White solid precipitated immediately as a fine suspension. The suspension was boiled for 15 min to facilitate filtration, and the solid was collected. Drying *in vacuo* at 80–100° provided 25.4 g (81%) of I as white solid, mp >250°.

2-Amino-4-chlorobenzenethiol Zinc Salt (II).—A mixture of 97 g (0.26 mole) of bis(4-chloro-2-nitrophenyl) disulfide (Aldrich Chemical Co., Milwaukee, Wis.), 2.6 l of glacial acetic acid, and 100 ml of concentrated hydrochloric acid was heated to 60°. External heating was discontinued and zinc dust (200 g, 3.1 g-atoms) was added in portions at a rate which kept the reaction temperature at 60–65°. During zinc addition the mixture turned from yellow to yellow-green and finally to pale pink. When addition was complete, the mixture was maintained at 60° for 1 hr and at reflux temperature for another hour. The crude zinc salt was filtered and dissolved in 2.5 l. of boiling N,N-dimethylformamide, and the solution was filtered to remove unreacted zinc dust.[9] The filtrate was poured into 5 l. of water and the resulting white suspension was allowed to stand at room temperature overnight. Filtration, air drying at room temperature, and final drying *in vacuo* gave 82.6 g (84%) of zinc salt II as a white solid, mp >300°.

2-Chloro-7-hydroxyphenothiazine (VII).—To a mixture of 100 g (0.26 mole) of the pulverized zinc salt II, 75 g (0.52 mole) of chlorohydroquinone (III), and 1 l of alcohol was added a solution of 21 g (0.52 mole) of sodium hydroxide in 175 ml of water. The mixture was heated at reflux and a rapid stream of oxygen was introduced below its surface for 1 hr. Filtration of the hot mixture provided a brown solid and dark brown filtrate. The filtrate was poured into 6 l of cold water containing 90 g of sodium hydrosulfite. The resulting light tan suspension was extracted with ether (three 600-ml portions) and the extracts were dried over a mixture of magnesium sulfate and sodium hydrosulfite. The ether was evaporated under reduced pressure and unreacted chlorohydroquinone was removed by pumping the residue at 120–125° and 0.05 mm. The remaining tan solid (mp 211–216°) was stirred for 0.5 hr with 220 ml of refluxing benzene in a nitrogen atmosphere. The resulting slurry was allowed to cool and was filtered. The solid was dried *in vacuo*, providing 81 g (62%) of VI, mp 223–226° (lit.[4] mp 224–226°). The identity of V was confirmed by infrared and mixture melting point comparison with an authentic sample prepared according to the four-step procedure of Kadaba and Massie.[4]

3-Hydroxyphenothiazine (VI).—The reaction between the zinc salt of 2-aminobenzenethiol (I) and chlorohydroquinone, carried out as described for the synthesis of VII (above), gave a 67% yield of 3-hydroxyphenothiazine, mp 175–177.5°. This material was identical (infrared spectrum and mixture melting point) with an authentic sample of VI made by thionation of 4-hydroxydiphenylamine and obtained as white scales (toluene), mp 177.5–178.5° (lit.[5] mp 170–175°; no yield or analysis reported).

Anal. Calcd for $C_{12}H_9NOS$: C, 66.93; H, 4.19; N, 6.51. Found (authentic sample): C, 67.17; H, 4.16; N, 6.53.

In a sealed, evacuated tube VI melted at 188.5–189°.

Acknowledgment.—The authors gratefully acknowledge the assistance of Sandra Graham and Mary Schlauter in carrying out these preparations.

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[6] N. Steiger, U. S. Patent 2,454,260 (Nov. 16, 1948).

[7] Modification of the method of K. J. Farrington and W. K. Warburton, *Australian J. Chem.*, **8**, 545 (1955).

[8] Microanalysis was performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

[9] The filtered zinc dust should be disposed of immediately. It begins to smoke on standing in air.

Halogenated Ketenes. I. Dichloroketene[1,2]

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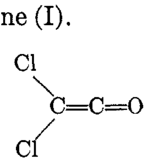
Owing to the rather recent interest in cycloaddition reactions of ketenes with various types of olefins and acetylenic compounds, and also because of the possibilities as a monomer for polymerization, it became of considerable interest to investigate the preparation of dichloroketene (I).



I

Until recently, all dihalogen ketenes were unknown. Difluoroketene[4] has recently been prepared and reportedly distils with ether. It has been reported that this material behaves like ketene and is practically impossible to separate from ether. Staudinger[5] attempted the synthesis of I by the thermal decomposition of the anhydride of dichloromalonic acid and

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[1] This work was supported by a National Science Foundation Grant (GP-4628) and a Faculty Research Grant, North Texas State University.

[2] Presented at the Southeast-Southwest Regional Meeting of the American Chemical Society, Memphis, Tenn., Dec 1965.

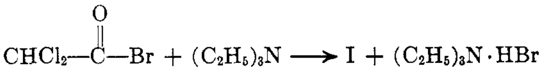
[3] To whom communications concerning this paper should be addressed.

[4] N. N. Yarovenko, S. P. Motornyi, and L. I. Kirenskaya, *Zh. Obsch. Khim.*, **27**, 2796 (1957).

[5] H. Staudinger, E. Anthes, and H. Schneider, *Ber.*, **46**, 3539 (1913).

diphenylketene. However, I could not be detected and it was concluded that this material was possibly produced but quickly polymerized under the reaction conditions.

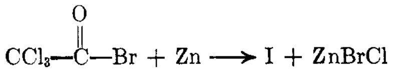
One of the oldest methods of preparing ketenes consists in the dehydrohalogenation of acid halides with tertiary amines.[6] Consequently, the dehydrobromination of dichloroacetyl bromide with triethylamine was investigated for the preparation of I. The de-



$$CHCl_2—\overset{O}{\overset{\|}{C}}—Br + (C_2H_5)_3N \longrightarrow I + (C_2H_5)_3N\cdot HBr$$

hydrobromination occurred as evidenced by the consumption of the acid halide and formation of triethylammonium bromide. However, I could not be detected and only a polymeric material was found to be present. Therefore, it was concluded that I was produced but immediately polymerized in the presence of the amine salt, since tertiary amine salts are known to catalyze the polymerization of some ketenes.[7,8]

The dehalogenation of trichloroacetyl bromide with zinc activated with copper was also investigated as a possible route to I and found to be very successful.



$$CCl_3—\overset{O}{\overset{\|}{C}}—Br + Zn \longrightarrow I + ZnBrCl$$

A molar ratio of zinc/acid halide of 3/1 to 5/1 has been found to be optimum, employing either anhydrous ether or dry ethyl acetate as solvent. This reaction goes to completion as evidenced by the consumption of all the acid halide as well as a stoichiometric loss of zinc. This ketene does not distil with ether like ketene and difluoroketene, nor does I distil with ethyl acetate or hexane. Numerous attempts to isolate I in the pure state were unsuccessful owing to the undesirable polymerization of this material. However, this was not surprising, since this seems to be characteristic of low molecular weight ketenes. The ketene was shown to be present in the reaction mixture by conversion with aniline to dichloroacetanilide. This new ketene was consistently prepared in yields of 60–70%.

The compound could be separated from the zinc halide and isolated in hydrocarbon solvents, such as hexane or octane. The presence of the ketene in hydrocarbon solvent was demonstrated by the formation of dichloroacetamide with ammonia. This ketene partially distils with octane and decane under reduced pressure.

An infrared spectrum of I which had distilled with octane was obtained. There was a band at 1940 cm^{-1}, which represents the stretching vibrations of the C=C=O group. This band appears at 2160 cm^{-1} in ketene and 2130 cm^{-1} in diphenylketene.[9,10] The infrared spectrum showed no evidence whatsoever of dimerization in the usual ketene fashion.

A hydrocarbon solution of I is a very convenient source of this new material as demonstrated by the preparation of N-benzyldichloroacetamide, a new compound. The ether or ethyl acetate solution from the reaction mixture is stable up to 1 week at 5° before any loss of ketene can be detected. A 2.5% solution of I in octane is stable under the same conditions and also at 85° for 24 hr with no loss of I.

Experimental Section

Dichloroacetyl bromide and trichloroacetyl bromide used in this investigation were prepared from the corresponding acids and phosphorus tribromide.[11]

Activation of Zinc.—A 4-g (0.016 mole) portion of hydrated copper sulfate was dissolved in 150 ml of water, and this solution was added to 60 g (0.92 g-atom) of zinc dust. This mixture was stirred for 2 hr. The zinc dust was removed by filtration and washed several times with acetone. The zinc was dried in a vacuum oven at 100° prior to use in the dehalogenation reaction.

Prepartion of I by Dehydrohalogenation.—Into a 250-ml flask equipped with a stirrer, reflux condenser, and a dropping funnel, were placed 150 ml of anhydrous ether and 37 g (0.19 mole) of freshly distilled dichloroacetyl bromide. A 24-g (0.24 mole) portion of triethylamine in 25 ml of ether was placed in the dropping funnel. This amine solution was then added dropwise to the vigorously stirred acid bromide solution. The triethylammonium bromide precipitated from the reaction solution during the addition. The amine salt was separated from the reaction solution by filtration, washed with ether, and dried. There was obtained 36.5 g of the hydrobromide. Treatment of an aliquot of the ether solution with aniline and also with ammonia did not result in the formation of any dichloroacetanilide or dichloroacetamide. Evaporation of the ether solution yielded 22.2 g of a black viscous material which could not be vacuum distilled.

Preparation of I by Dehalogenation.—Into a 250-ml flask equipped with a stirrer, reflux condenser, and a dropping funnel, were placed 26 g (0.40 mole) of zinc dust activated with copper and 150 ml of absolute ether. A solution of 30 g (0.13 mole) of freshly distilled trichloroacetyl bromide in 15 ml of ether was added dropwise to the stirred mixture. At the conclusion of the exothermic reaction, the ether solution was separated from the unreacted zinc. There was a loss of 8.6 g of zinc. This ether solution was treated with an excess of aniline and washed successively with dilute hydrochloric acid and water. Upon recrystallization this anilide had a melting point of 116–117° (lit.[12] mp 117°). A mixture melting point with an authentic sample of dichloroacetanilide showed no depression.

Isolation of I in a Hydrocarbon Solvent.—A 100-ml portion of a I reaction solution containing 6.9 g of I was vigorously stirred while 100-ml of octane was added dropwise. This resulted in the precipitation of the zinc halide. After the addition, the octane solution was separated from the precipitated zinc halide with a pipet. An additional 100 ml of octane was then added to the zinc halide residue, and with stirring this mixture was heated to 60–70°. After 30 min the octane solution was removed and combined with the original extract. The ether was removed by distillation to yield an octane solution containing 2.5% of I. Saturation of this solution with ammonia resulted in the formation of 5.1 g of dichloroacetamide, which upon recrystallization had a melting point of 96° (lit.[13] mp 96°).

Distillation under reduced pressure of 100 ml of a decane solution containing 2.5 g of I yielded a decane distillate containing 0.75 g of I. Numerous efforts to distil I in the absence of solvent were unsuccessful.

An infrared spectrum of an octane solution of I was obtained and showed the characteristic absorption of C=C=O at 1940 cm^{-1}.

Preparation of N-Benzyldichloroacetamide from I.—An excess of benzylamine in ether was added to a 100-ml portion of a 2.5% solution of I (0.02 mole) in octane. The resulting solution was washed with dilute hydrochloric acid and finally water. Upon drying and evaporation of the solvents, there was obtained 4.7 g (96%) of a white crystalline solid, mp 93–94.5°. Recrystallization gave a melting point of 95–96°.

Anal. Calcd for $C_9H_9Cl_2NO$: C, 49.56; H, 4.16; N, 6.42. Found: C, 49.81; H, 4.37; N, 6.26.

Assay Procedure for Hydrocarbon Solutions of I.—An aliquot of a hydrocarbon solution of I was treated with a large excess of water and vigorously shaken in a separatory funnel. The

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[6] H. Staudinger, *Ber.*, **40**, 1148 (1907).

[7] H. Staudinger and H. W. Klever, *ibid.*, **41**, 594 (1908).

[8] J. C. Sauer, U. S. Patent 2,238,826 (1941); *Chem. Abstr.*, **35**, 4970 (1941).

[9] D. H. Whiffen and H. W. Thompson, *J. Chem. Soc.*, 1005 (1946).

[10] L. G. Drayton and H. W. Thompson, *ibid.*, 1416 (1948).

[11] F. E. King and P. C. Spensley, *ibid.*, 2144 (1952).

[12] C. O. Cech, *Ber.*, **9**, 337 (1876).

[13] L. Bisschopinck, *ibid.*, **6**, 731 (1873).

aqueous layer containing dichloroacetic acid was titrated with a standard solution of sodium hydroxide. The results of this assay procedure are in good agreement with the older method of conversion to an amide and are more reproducible and more efficient.

Formation of Heneicosane-2,4-dione by Acid-Catalyzed Rearrangement of Isopropenyl Stearate

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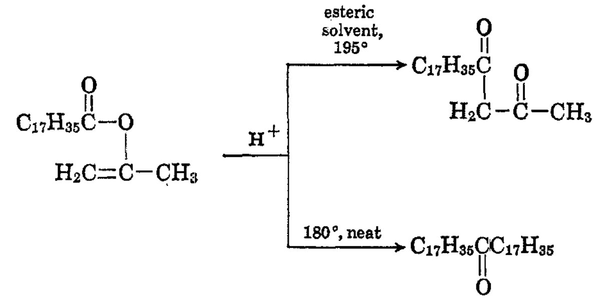
We have used the enol ester, isopropenyl stearate, as an effective stearoylating agent.[2] The sole by-product, acetone, is driven off as a gas, thereby driving reaction to completion. Since even so weakly protonic a substance as N-methylstearamide is stearoylatable by such a procedure, we considered that diethyl malonate should also stearoylate at the active methylene group on refluxing the reactants together in the presence of the usual trace of acid catalyst.



An anomalous crystalline reaction product having double melting points at 70 and 75° was obtained in 70% yield instead. Acetone, although evolved and collected, was formed in a molecular proportion of only about 10% of the expected value. At first we thought that the unexpected compound might be the O-acylation product, since the infrared spectrum showed carbonyl region bands at 1774, 1737 (intense), and 1644 cm^{-1}, the latter band presumed to be indicative of olefinic unsaturation. In accord with this, the substance was found to absorb strongly in the ultraviolet at 298 mμ. However, the elemental analysis precluded such a supposition and showed the product to be isomeric with isopropenyl stearate. The same isomeric product was also obtained when methyl stearate was used as the quasi-reactant instead of diethyl malonate, suggesting that all portions of the new molecule are constructed from isopropenyl stearate only.

From this and other data it is apparent that the product melting at 70 and 75° is the rearrangement product heneicosane-2,4-dione, $C_{17}H_{35}COCH_2COCH_3$. A search of the literature uncovered previous reports of such a rearrangement carried out pyrolytically at 500° on short-chain molecules.[3-5] Ultraviolet photochemical rearrangement of enol esters to β-diketones has also succeeded, but products obtained by photochemical change on a given substrate may be different from those obtained pyrolytically.[6] Feldkimel-Gorodetsky and Mazur have shown, for example, that 1-benzoyloxycyclohexene gives the ring-cleavage product, 1-benzoyl-5-hexen-2-one on irradiation, but gives 2-benzoylcyclohexanone on pyrolysis. Ritchie and Yousufzai[5] have presented evidence for a four-membered transitional cyclic compound, and Finnegan and Hagen[7] have shown a formal resemblance to the Fries rearrangement.

Since the "solvent" diethyl malonate or methyl stearate played no apparent role in the rearrangement, an experiment was carried out without solvent. By this means, we hoped to avoid the technical separation difficulties in removing high-boiling diethyl malonate and by-product ethyl stearate[8] formed by ester interchange. For this reason, isopropenyl stearate was held molten at 200° for 1 hr with a catalytic amount of *p*-toluenesulfonic acid in the expectation of obtaining heneicosane-2,4-dione in nearly pure form. Surprisingly, the β-diketone was, to the contrary, formed in only small amount, the major product being stearone, formed in high yield.

To exclude the dilution effect from consideration in accounting for the different products, we heated isopropenyl stearate with acid catalyst substituting a volume of Nujol, an inert high-boiling hydrocarbon, equal to that of the previously used diethyl malonate. Although acetone evolution did occur, no β-diketone at all formed in 20 min at 185° and only traces of β-diketone formed at 200° during 1-hr heating. In the former case, unchanged starting material and an unknown substance absorbing at about 1815 cm^{-1} were found. At the higher temperature and longer reaction time, the starting isopropenyl stearate was completely consumed, but only trivial amounts of heneicosanedione and stearone were formed, together with increased amounts of the 1815-cm^{-1} absorbing substance which appears not to be an anhydride. In view of the three different results in the three different media, the solvent effect cannot be ignored.

A reviewer has called our attention to the wide deviation of the infrared and ultraviolet absorption data of our heneicosane-2,4-dione, $\bar{\nu}_{max}^{CS_2}$ 1737 cm^{-1}, $\lambda_{max}^{isooctane}$ 298 mμ (ε 3000), from that of acetylacetone which absorbs 1530 to 1640 cm^{-1} (broad) with a weaker band at 1709 cm^{-1} and exhibits λ_{max} 271 mμ. This apparent discrepancy merely reflects the existence of tautomeric forms. Acetylacetone exists principally in the chelated-ring, monoenolic form while our fatty acid compound apparently exists mainly in the β-diketonic tautomeric form. The band differences have been used by previous workers in measuring the

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(1) Eastern Utilization Research and Development Division, Agricultural Research Service, U. S. Department of Agriculture.

(2) E. S. Rothman, S. Serota, and D. Swern, *J. Org. Chem.*, **29**, 646 (1964).

(3) F. G. Young, F. C. Frostick, Jr., J. J. Sanderson, and C. R. Hauser, *J. Am. Chem. Soc.*, **72**, 3635 (1950).

(4) R. J. P. Allan, J. McGee, and P. D. Ritchie, *J. Chem. Soc.*, 4700 (1957).

(5) P. D. Ritchie and A. H. K. Yousufzai, *Chem. Ind.* (London), 1918 (1964).

(6) M. Feldkimel-Gorodetsky and Y. Mazur, *Tetrahedron Letters*, 369 (1963).

(7) R. A. Finnegan, and A. W. Hagen, *Tetrahedron Letters*, 365 (1963).

(8) R. L. Adelman [*J. Org. Chem.*, **14**, 1057 (1949)] reported ester interchange in vinyl and isopropenyl esters as being highly unusual.