

SYNTHESIS AND REACTIONS OF 3,3,3-TRICHLORO-2-METHYL-1-PROPENE
AND OF 1,1,3-TRICHLORO-2-METHYL-1-PROPENE

by

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B. S., Kansas State College of
Agriculture and Applied Science, 1954

A THESIS



submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

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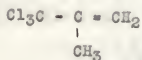
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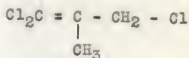
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STATEMENT OF THE PROBLEM

The chief purpose of this investigation was to study certain new lines of chemistry of 3,3,3-trichloro-2-methyl-1-propene (TMP) and 1,1,3-trichloro-2-methyl-1-propene (allyl-TMP). The structural relationships of these compounds are shown by their formulas.



TMP



allyl-TMP

It will be observed that allyl-TMP is the allylic isomer of TMP. The chemistry of these compounds is of unusual interest in the light of recent work carried out by de la Mare (1).

The above general statement of the problem may be divided into more specific problems as follows:

The dehydration of 1,1,1-trichloro-2-methyl-2-propanol (chlorethane). This study was needed to expand the scope of amines useful as additives for forming catalysts in the dehydration of chlorethane. Pledger (12) found that quinoline was useful for this purpose.

A study of the reactions of TMP and allyl-TMP with malonic ester, substituted malonic esters and acetoacetic ester for the purpose of forming the new dichloromethylallylated derivatives of these substances. $\text{Cl}_2\text{C} = \text{C} - \text{CH}_2$ represents dichloromethyl-allyl group as present in allyl-TMP.

A study of the condensation of the dichloromethylallylated malonic esters with urea to give the corresponding new barbiturates.

HISTORICAL BACKGROUND

A search of the literature revealed that both TMP and allyl-TMP had been investigated to only a limited extent. Practically no work is reported to have been done with these substances in the field of nucleophilic type replacement reactions. The two isomers are unusual in that TMP may rearrange to allyl-TMP but the reverse rearrangement has never been reported. This failure of the allyl-TMP to rearrange may be attributed to the chlorine atoms located on the terminal carbon of the double bond. The inductive effect of these chlorines is such as to prevent isomerization to TMP. Hatch and Russ (4) studied the rate of replacement of the chlorine of several allylic chlorides by iodine using potassium iodide in acetone. They found that allyl-TMP reacted 33 times as fast as allyl chloride. Hatch and Alexander (5) studied the rate of replacement of chlorine in the same set of allylic chlorides by ethoxide ion in ethyl alcohol. Allyl-TMP was more reactive (17.5 times) than allyl chloride. These results show that 2 vinyl chlorides aid these two displacements.

Until the time of the investigation by Pledger (12) there existed no dependable method for synthesis in high yield (above 50 per cent) of highly purified TMP. 3,3,3-trichloro-2-methyl-1-propene was first reported by Jacob (7) in 1940. He synthesized TMP, b.p. 132°C, R.I. 1.479, D 1.293 in 15 per cent

conversion yield using phosphorus pentoxide in the presence of N,N-dimethylaniline. He also obtained a 57 per cent conversion to the allylic isomer 1,1,3-trichloro-2-methyl-1-propene (allyl-TMP) along with 15 per cent conversion yield of alpha-chloro-isobutyric acid.

Later Price and Marshal (14) modified this procedure. They employed two moles of quinoline rather than one equivalent of dimethylaniline. In this manner they were able to obtain a 30 to 43 per cent conversion yield to TMP. However, their procedure had definite disadvantages. The reaction mixture swelled, often into the delivery tube of the flask, and the clogging in larger runs often caused minor explosions.

As late as 1952 de la Mare and Vernon (1) reported that only 13 grams (3 per cent yield) of purified TMP from 400 grams of chloretonone could be obtained by the method of Jacob. They also stated that the method of Price and Marshal gave even worse yields than that of Jacob.

McElvain and Stevens (10) reported dehydrating chloretonone using three moles excess of thionyl chloride. In only one reaction carried out, they reported a 93 per cent yield of TMP, b.p. 130-137°C, by refluxing for eight hours. No essential details were given of the condition of the thionyl chloride used. However, the reported yield could not be reproduced.

Pledger (13) and Ott (11) described a method whereby quinoline-purified thionyl chloride could be used effectively. They reported, however, the product was sometimes contaminated with starting alcohol and its chloride. These workers likewise

found a 30 hour reflux period was necessary.

EXPERIMENTAL

Apparatus

Apparatus for the Dehydration of Chlorotone. The apparatus consisted of a three-neck, round-bottom flask with standard taper joints equipped with thermometer and a water cooled condenser vented into the hood. Measurement of rate of flow of exhaust gases was carried out by passing the gases liberated into a flask containing 10 milliequivalents of a sodium hydroxide solution and rating the time required for neutralization using phenolphthalein as an indicator. The reaction vessel was heated by a bath of cottonseed oil.

Apparatus for the Synthesis of 3,3-Dichloro-2-methylallyl-substituted-malonic esters and Barbiturates. The apparatus was a four-neck, round-bottom flask with standard taper joints equipped with a thermometer, motor-driven ground-glass stirrer, a water-cooled condenser and a dropping funnel for adding liquid reagents. Calcium chloride drying tubes on the condenser and dropping funnel protected the reaction mixture from moisture. The source of heating was an electrically controlled gas-coal heating mantle.

Apparatus for the Distillation of the Reaction Mixture from Dehydration. Separation of reaction products was accomplished by employing a glass-helices-packed column (300 mm in length and 20 mm in diameter), a standard head, and a condenser, etc. for distillation.

Apparatus for Solvent Removal. This apparatus was a total-

reflux, variable-take-off still head connected to the reaction flask. A calcium chloride drying tube was connected to one of the stopcocks to protect the distillate from moisture. Receiving flasks were attached to the still head by a rubber stopper as needed.

Apparatus for Reduced Pressure Distillation. K-column for Fractionation. This apparatus consisted of a suitable size two-neck, round-bottom flask connected to a glass-helices-packed column (120 mm in length and 20 mm in diameter) provided with an electrical heating element used for maintaining adiabatic conditions. A total-reflux, variable-take-off still head containing the necessary stopcocks for cutting fractions under reduced pressure was attached to this K-column.

Fifty-milliliter Erlenmeyer flasks were attached to the still head by a rubber stopper and served as clean distillate receivers for storing and handling. A Hi-vac oil pump with a McLeod manometer was used in most cases. A trap immersed in dry ice-acetone and a potassium hydroxide trap were inserted between the pump and the still head. The traps seemed to protect the pump from volatiles and hydrogen chloride. A heated Crisco bath was used for heating the pot on the still.

Abbreviations

Refractive indices in this thesis were determined at 20° C using the D line of sodium and will be abbreviated by the symbols R.I.

Densities reported in this thesis were determined at 20° C

referred to water at 4° C and will be abbreviated by the symbol D.

Molecular refraction and saponification equivalent reported in this thesis will be abbreviated by the symbols MR and S.E. respectively.

Synthesis of 3,3,3-Trichloro-2-methyl-1-propene
by Adding Amines to Form Catalysts

General Procedure. To the necessary apparatus was added 186.5 g (1.0 mole) of hydrated chlorethane and 2 to 70 millimoles of various amines. Then 290 ml. (4.0 moles) of Hooker technical refined grade of thionyl chloride was added slowly because of initial reaction between thionyl chloride and the water of hydration of chlorethane. The mixture was then heated to the reflux temperature (79° C) of thionyl chloride and maintained at this temperature until the neutralization times, taken in one hour intervals, indicated that the rate of gassing had decreased to one-tenth of the previous steady state rate, or to relatively nil. The reaction was stopped by cooling the reaction flask in an ice bath. The mixture was subjected to fractional distillation at atmospheric pressure. The fraction, b.p. 80-129° C was poured over ice, washed with aqueous sodium carbonate, dried over anhydrous potassium carbonate, filtered and found to be TMP and added to the TMP fraction b.p. 129-139° C, R.I. 1.4795. The fraction 139-155° C was a mixture of TMP and 1,1,3 trichloro-2-methyl-1-propene (allyl-TMP). The composition of the latter fraction was determined from a curve of R.I. versus per cent TMP

in the binary mixture of TMP and allyl TMP. The yields obtained from various amines used in varying concentrations are listed in Table 1.

Effect of Impurities on the Dehydration of Chlorethane

To a flask of appropriate size was added 181 g (1.02 mole) of chlorethane and 962.6 mg (12.4 millimole) pyridine. Then 300 ml. (4.04 moles) of purified thionyl chloride containing 107.3 mg (0.66 millimole) ferric chloride and 162.2 mg (1.22 millimole) aluminum chloride as impurities was added. The general procedure for dehydration was followed. Reaction time was 5.5 hours.

Distillation of the reaction mixture gave an overall yield of 82 per cent. The yield of TMP, b.p. 130-140° C, R.I. 1.4805 was 73 per cent. The residue of TMP and allyl-TMP was nine per cent.

Synthesis of the Chlorosulfinic Ester of Chlorethane

The apparatus for this synthesis was composed of a two-liter four-neck flask fitted with a thermometer and a reflux condenser.

Five hundred milliliters of dry carbon tetrachloride, 145 ml. (2.0 mole) of purified thionyl chloride, 177.5 g (1.0 mole) anhydrous chlorethane and 5 ml. (6.0 mole per cent) of pyridine were introduced into the flask. The liquid mixture was heated slowly by an oil bath. When the temperature of the mixture reached 50° C, hydrogen chloride began to be evolved rapidly and dissolved in the trap. The temperature was raised slowly to 76° C over a one-hour period.

Table 1. Yields, amines used and conditions for dehydration of chlorethane.

Run:	Amine or salt used	Mole % of amine	Reflux time hrs.	TMP yield	Allyl-TMP yield	Total
1	Aniline	6.3	7.5	79	0	79
2	Aniline-HCl	2.4	10	78	10	88
3	Mono-t-Butyl amine	0.7	6.5	79	0	79
4	Mono-t-Octyl-amine	0.7	6.5	74	6	80
5	Same ^a	0.7 ^a	8	68	11	79
6	Same	0.23	7	55	23	78
7	Di-n-butyl amine	4.0	6	78	0	78
8	Piperidine	1.0	7	79	9	88
9	Diphenylamine	3.5	7.5	76	6	82
10	N,N-Dimethyl-aniline	5.5	9	83	0	83
11	Triethylamine	5.0	7.5	83	0	83
12	Pyridine	1.24	6	83	8	91
13	Quinoline	0.9	22 ^b	76	0	76
14	Same	6.9	7.5	66	9	75
15	Tetraethylammonium iodide	1.3	8	0	88	88
16	Tetramethylammonium chloride	2.0	7.5	82	2	84
17	Ammonia	23.5 ^b	12.5	59	0	59 ^c

^aLast two-thirds of amine added after one-third of reaction time was gone.

^bNo neutralization taken on this run.

^cRemainder was largely unconverted chlorethane.

At the end of the one hour interval very little hydrogen chloride was evolving and drops of an insoluble oil floated on the surface of the mixture. The mixture was cooled with an ice bath. Titration of an aliquot of the trap water showed that 1.09 moles of hydrogen chloride was evolved during the reaction. The insoluble oil was removed from the cooled mixture by a pipette. The clear liquid was placed under water aspirator vacuum. This brought about complete removal of volatile liquids and left white needle crystals of the chlorosulfinic ester of chloretone. This material weighed 251 g (98 per cent yield) and had m.p. 53-56° C in a sealed tube.

A 200-milligram sample of the needles was weighed as rapidly as possible while taking precautions to keep exposure to air at a minimum. Ten milliliters of absolute ethyl alcohol was added and the dissolved sample titrated with standard sodium hydroxide. This procedure gave a neutralization equivalent of 257 (calculated 260).

A control experiment without pyridine run under the same conditions required eight hours to go to completion. The yield of product was 97 g (73 per cent) of inferior quality contaminated with TMP.

Thermal Decomposition of Chlorosulfinic Ester of Chloretone

No solvent. The chlorosulfinic ester of chloretone, 65 g (0.25 moles) was heated by a heating mantle to a temperature of 80° C. The gas liberated during the decomposition was trapped in 500 ml. of water. At the end of 23 hours little gas was being

evolved. Titration of an aliquot of the trap water showed that 0.58 equivalent of acidic gas had been liberated.

Distillation of the mixture gave 27.0 g of TMP, b.p. 130-136° C, R.I. 1.4785-1.4808, 9.05 g of a mixture of TMP and allyl-TMP, b.p. 136-150° C, R.I. 1.4868. This corresponded to a 79 per cent yield of TMP and 10 per cent allyl-TMP.

With solvent. One hundred and twenty-five grams (0.49 moles) of the chlorosulfinic ester of chloretone was dissolved in 107 ml. (1.5 moles) of thionyl chloride. To the mixture was added 2.5 ml. (3.0 mole per cent) of pyridine. The mixture was heated to 80° C. The gas liberated during the decomposition was trapped in 500 ml. of water. The reaction was followed by titration of aliquots taken at regular intervals. At the end of 7 hours reflux time, 1.24 equivalents of gas had been trapped, and further titration gave a somewhat constant value.

Distillation of the reaction mixture gave a conversion yield of 78.4 per cent TMP and two per cent allyl TMP.

A control experiment (without pyridine) carried out simultaneously with the same moles, same amounts of ester and solvent liberated 0.96 equivalents of acidic gas. Distillation gave a yield of 50 per cent TMP and 29 per cent allyl-TMP. It was possible that this was not a true control as some catalyst may have been absorbed on the chlorosulfinic ester.

Synthesis of Diethyl Dichloromethylallylmalonates

General Procedure. To the necessary apparatus was added 500 ml. of anhydrous ethyl alcohol. Sodium metal was added

slowly in pea-size pieces to prepare sodium ethoxide in situ. To the stirred mixture was added the malonic esters over a period of 0.5 hour up to 1.75 hour, then TMP was added dropwise over a period of two to three hours. The mixture was refluxed for an additional two to 18 hours. The excess solvent was removed, the residue diluted with water and the organic layer separated. The aqueous layer was extracted with ether and the extract combined with the organic layer. The ether fraction was dried over anhydrous magnesium sulfate and filtered. The ether was removed on a steam cone and the residual liquid subjected to distillation under reduced pressure using the K-column described previously.

Synthesis of Diethyl 3,3-Dichloro-2-methylallylmalonate (I)

Using TMP. By the general procedure 25.3 g (1.1 mole) sodium, 158.3 g (0.995 mole) diethyl malonate and 159.5 g (1.00 mole) TMP were reacted for four hours and 15 minutes at 80° C. The residual liquid weighed 275 g. A 200 g aliquot was taken for distillation and gave (a) 25.7 g of unreacted diethyl malonate (18 per cent); (b) 83.0 g of diethyl 3,3-dichloro-2-methylallylmalonate (I) b.p. 95° (0.2mm)- 100° C (0.3 mm), R.I. 1.4672-1.4678; (c) 58.6 g of residue which solidified on standing. The residue was recrystallized from absolute ethanol and yielded 36.5 g of white crystals, m.p. 66-67° C. A second and third crop was recovered which weighed 11.8 g and 3.5 g respectively and had the same melting points as the first crop. This solid was the disubstituted malonic ester, diethyl bis(3,3-dichloro-2-methyl-allyl)-malonate (II). (See anal. below).

The conversion yield to the monosubstituted ester I was 53 per cent while that of the disubstituted II was 20 per cent.

Synthesis of Diethyl 3,3-Dichloro-2-methylallylmalonate (I)

Using allyl-TMP. The general procedure for the preparation of diethyl 3,3-dichloro-2-methylallyl-substituted malonates was used. The allyl-TMP was added over a period of two hours at room temperature and the mixture refluxed two hours and 30 minutes. The temperature of the mixture increased from 25° C to 45° C during the addition of allyl-TMP because of heat of reaction of the reactants. Twenty-three and one-half g (1.07 moles) of sodium, 172.7 g (1.07 moles) of diethyl malonate and 159.5 g (1.00 mole) of allyl-TMP gave the following results: (a) 41.88 g of recovered diethylmalonate; (b) 172.6 g (62.5 per cent conversion) of (I), diethyl 3,3-dichloro-2-methylallylmalonate, b.p. 105° (0.6 mm) or 122° C (1.0 mm), R.I. 1.4679; (c) 40.8 g residue from which was recovered 31 g of diethyl bis(3,3-dichloro-2-methylallyl)malonate (II), m.p. 66-67.5° C.

<u>Anal.</u> Calcd. for (I) $C_{11}H_{16}O_4Cl_2$:	C, 46.76; H, 5.70; Cl, 25.04
Found:	C, 46.82; H, 5.45; Cl, 24.88
Calcd. for (II) $C_{15}H_{20}O_4Cl_4$:	C, 44.36; H, 4.96; Cl, 34.93
Found:	C, 44.43; H, 4.74; Cl, 34.40

One-Step Synthesis of Diethyl bis(3,3-dichloro-2-methylallyl)malonate (II). To 25 g (1.09 moles) sodium in 500 ml. anhydrous ethyl alcohol was added 80.2 g (0.5 mole) of diethyl malonate and 168 g (1.09 moles) of TMP as before. The mixture was refluxed

for 18 hours, filtered and the salt cake washed with hot anhydrous ethyl alcohol. The salt cake weighed 63 g. The excess alcohol was removed by distillation. The oily residue weighing 206 g solidified on standing. It was taken up in a minimum of hot absolute ethyl alcohol and allowed to crystallize. Filtration gave 102.1 g of white crystals, m.p. 66-67° C. A second crop weighed 26.9 g, m.p. 65-67° C. The residual liquid from crystallization was subjected to distillation at reduced pressure. This gave: (a) 13.8 g of monosubstituted malonic ester, b.p. 100° C (1.5 mm), R.I. 1.4643; (b) 13.2 g of intermediate fractions b.p. 118° (2.4 mm)-142° C (2.0 mm), R.I. 1.4780-1.4870; and (c) 14.1 g of the disubstituted malonic ester, b.p. 150° C (2.0 mm) which solidified on standing.

The total weight of diethyl bis(3,3-dichloro-2-methylallyl) malonate (II) obtained by this changing of conditions was 143.1 g (71 per cent conversion yield). The yield of diethyl 3,3-dichloro-2-methylallylmalonate (I) was reduced to 10 per cent conversion while a 6.4 per cent by weight mixture of the two was also obtained.

Using 1,1,3-trichloro-2-methyl-1-propene (allyl-TMP) under essentially the same reaction conditions gave a 76.1 per cent conversion yield of the disubstituted malonic ester (II).

Synthesis of Diethyl Methyl-(3,3-dichloro-2-methylallyl)-malonate (III). By the general procedure 25.8 g (1.13 moles) sodium, 197.4 g (1.13 moles) of diethyl methylmalonate and 192.5 g (1.21 moles) TMP were reacted for two hours and 15 minutes at 25-30° C and two hours and 30 minutes at 80° C. The residue

taken for distillation weighed 297.3 g. Distillation gave 30.7 g (16 per cent recovery) of starting diethyl methylmalonate. A total of 206.4 g of diethyl methyl-(3,3-dichloro-2-methylallyl)-malonate (III), b.p. 96° (0.3 mm)- or 110° C (1.1 mm), R.I. 1.4675-1.4680 was obtained. A heart cut with constants R.I. 1.4677 and D. 1.160 was taken for analyses. A residue of 24.5 g remained.

The conversion yield of diethyl methyl-(3,3-dichloro-2-methylallyl)malonate was 61.4 per cent, the recovery yield based on diethyl malonate 72.6 per cent. Explanation for the analytical data below is given in the DISCUSSION.

Anal. Calcd. for: $C_{12}H_{18}O_4Cl_2$: C, 48.5; H, 6.1; Cl, 23.9

Found: C, 49.6; H, 6.4; Cl, 26.2

Synthesis of Ethyl 3,3-Dichloro-2-methylallylacetate (IV)

The same general procedure as for the preparation of the diethyl dichloromethylallyl-substituted-malonates was followed. The reaction was carried out for three hours and 30 minutes at room temperature and for four hours at 80° C. Forty-nine g (2.13 moles) of sodium, 800 ml. anhydrous ethyl alcohol, 260 g (2.00 moles) of acetoacetic ester, and 335 g (2.1 moles) of TMP gave on distillation: (a) 36.9 g of forerun which was a mixture of reactants and did not exhibit a constant R.I. or b.p.; (b) 217 g (51 per cent conversion) of ethyl 3,3-dichloro-2-methylallylacetate (IV), b.p. 91° (2.1 mm)- 72.5° C (0.8 mm), R.I. 1.4705-1.4716, (c) 13.1 g (3.5 per cent conversion) of ethyl alpha, alpha-(3,3-

dichloro-2-methylallyl)acetoacetate (V) b.p. 135° (1.7 mm)- 140.5° C (1.0 mm), R.I. 1.5030.

Anal. for (IV). $C_8H_{12}O_2Cl_2$

Calcd.: C, 45.52; H, 5.73; Cl, 33.60; MR, 50.06; S.E. 211
Found : C, 45.34; H, 5.80; Cl, 34.14; MR, 50.66; S.E. 204

Anal. for (V). $C_{14}H_{18}O_3Cl_4$

Calcd.: C, 44.70; H, 4.82; Cl, 37.71
Found : C, 44.48; H, 4.78; Cl, 38.27

Syntheses of 5-(3,3-Dichloro-2-methylallyl)-5-Substituted-Barbituric Acids

To the necessary apparatus was added sufficient anhydrous alcohol and sodium to prepare the sodium ethoxide. To this stirred solution was added dichloromethylallylmaleonic ester followed by dry urea dissolved in a minimum amount of hot absolute alcohol. The mixture was refluxed from 5.5 to 35.5 hours. The reactants were added in equimolar amounts.

The solvent alcohol was removed, the mixture diluted with water and ether extracted. The ether extract was dried over anhydrous magnesium sulfate, filtered and ether removed on a steam cone. The residue remaining was unreacted starting material. The aqueous layer was acidified with hydrochloric acid. The solid which separated out was the desired barbiturate. After filtration the barbiturate was recrystallized from an ethyl alcohol-water mixture. When a solid separated from the original reaction mixture, it was filtered, dissolved in minimum amount of hot water, acidified and treated in the same manner as described above.

The results of these syntheses and the physical properties of

the barbituric acids are given in Tables 2 and 3.

Table 2. Syntheses of 5-substituted-5-(3,3-dichloro-2-methylallyl)barbituric acids.

Barbi- turic : Acid :	Malonic ester used	: Moles : : ester : :	Barbi- turic : Acid : grams :	% yield ^a
VI	3,3-Dichloro-2-methylallyl	0.80	91.8	46
VII	Bis(3,3-Dichloro-2-methylallyl)	0.48	19.6	11 ^b
VIII	(3,3-Dichloro-2-methylallyl)methyl	0.38	59.0	58 ^c

^aThe yield given is conversion yield.

^bA larger excess of solvent was used, in order to add a solution of the starting ester to the reaction mixture.

^cSodium methoxide was used as condensing agent and sec-amyl alcohol used as solvent.

Table 3. Physical properties of the barbiturates synthesized.

Properties	: Observed	: Value calculated
5-(3,3-Dichloro-2-methylallyl)barbituric Acid (VI)		
Melting point	229-231° C	
Per cent carbon	38.37	38.42
Per cent chlorine	28.6	28.4
Per cent nitrogen	10.8	11.2
5,5-(3,3-Dichloro-2-methylallyl)barbituric Acid (VII)		
Melting point	194-195° C	
Per cent carbon	38.60	38.53
Per cent chlorine	37.5	37.9
Per cent nitrogen	7.5	7.5
5-Methyl-5-(3,3-Dichloro-2-methylallyl)barbituric Acid (VIII)		
Melting point	192.5-194° C	
Per cent nitrogen	10.2	10.5
Per cent chlorine	25.9	26.7

DISCUSSION OF THE RESULTS

Synthesis of 3,3,3-Trichloro-2-methyl-2-propene by
Adding Amines to form Catalysts

Conversion of 1,1,1-trichloro-2-methyl-2-propanol (chlore-tone) into 3,3,3-trichloro-2-methyl-1-propene (TMP) involves the over-all chemical change represented by the following equation:



Until Pledger's (12) recent discovery of catalysis by addition of a minute quantity of amine, the above reaction was frequently found to occur only when exceedingly rigorous precautions and purifications of starting materials were carried out.

The author had spent considerable time on a senior research problem in an attempt to prepare TMP by the use of thionyl chloride. Modifications of the McElvain and Stevens procedure were devised but the yields were seldom as high as desirable. A given procedure might work fine for purified thionyl chloride yet fail completely when the technical refined grade was used. Even drastic differences in yields of TMP were noted between uses of purchased batches of purified grades of white label thionyl chloride. Often 1,1,1,2-tetrachloro-2-methylpropane was found as an undesirable impurity in the allyl-TMP fraction. Ikenberry (6) found that by using small amounts of Lewis acids such as ferric chloride and aluminum chloride in the above

reaction, the tetrachloromethylpropane could be obtained in almost quantitative yields. As these Lewis acids were present in varying traces in the technical thionyl chloride, it was not surprising that erratic yields were obtained by the use of this reagent.

Gerrard and French (3) investigated the interaction of thionyl chloride and hydroxy compounds such as iso-amyl, n-butyl alcohol and ethyl lactate. They observed that less than 0.1 mole of tertiary amine or its hydrochloride was sufficient to cause formation of the chloride from the corresponding hydroxy compounds in yields approaching 95 per cent. Since Pledger (12) likewise used tertiary bases, but got instead dehydration, it appears that the inductive effect of the three chlorine atoms makes chlorotone behave differently from a typical alcohol.

It was found that the catalyst in the dehydration was not limited to the use of only a tertiary base. Primary amines would work just as well. Aniline was introduced into the reaction both as the free amine and as its hydrochloride salt with no reduction of yield of TMP. The somewhat longer reaction time and higher percentage of allyl-TMP was probably caused by differences in concentration of catalyst.

A series of reactions using mono-t-octylamine seemed to indicate there was a minimum effective concentration of catalyst. Adding the amine in varying amounts seemed to influence the ratio of TMP to allyl-TMP. Using 0.7 mole per cent of amine there was isolated 74 per cent TMP and 6 per cent allyl-TMP. When the concentration of the amine was decreased to 0.23 mole per cent there was an increase in the formation of allyl-TMP from 6

per cent to 23 per cent yield. If, however, 0.23 mole per cent of the amine was added initially and an additional 0.46 mole per cent added after three hours of reaction time, the yield of allyl-TMP decreased by approximately one-half (11 per cent). This definite effect on yields of allyl-TMP is suggestive that possibly the amine salt, in part, acts by forming a type of metastable complex with the Lewis acids present as impurities. This is probably a minor effect, and the main specie of catalyst is probably the RNH_3^+ cation or in general RNR_3^+ where the latter R is one or more H's.

The secondary amines used, piperidine and diphenylamine, stood at opposite ends of the basicity scale. The effect due to degree of basicity must have been quite small for the yields realized from them were nearly equivalent. Diphenylamine, although a weak base, forms salts with strong acids. On addition of the amine to thionyl chloride a deep blue coloration occurred, which persisted throughout the length of reaction. Similar blue colors are observed when oxidizing substances are added to diphenylamine in sulfuric acid. This evidence helps to give support to a theory that an unknown complex is involved. However, its effect must be slight and dominated by the main specie of catalyst mentioned since the yields are nearly equivalent whether a deep blue coloration occurs, or whether it doesn't.

The scope of tertiary amines was further established. Besides quinoline and pyridine used by Pledger, triethylamine and N,N-dimethylaniline gave about the same results. The yields of TMP were slightly higher than when primary and secondary amines

were used.

Up to this point it can be seen that the following species of ions: $\text{RNH}_3^+ \text{Cl}^-$, $\text{R}_2\text{NH}_2^+ \text{Cl}^-$, $\text{R}_3\text{NH}^+ \text{Cl}^-$ exist in solution in significant excess of any Lewis acids present in thionyl chloride and these ions probably act as the catalyst. Possibly some coordinate dipolar complex with the traces of Lewis acids present in technical refined thionyl chloride, is also involved by an alternative and simultaneous path of catalysis. However, this complex is not necessarily needed and may be ignored, since essentially the same catalytic results were obtained in the complete absence of the Lewis acids. This occurred when Matheson white label thionyl chloride, or laboratory quinoline-purified thionyl chloride was used. Perhaps further study of the role of quaternary salts as catalysts would aid in clarifying further the role of the catalyst.

Two quaternary salts, tetraethylammonium iodide and tetramethylammonium chloride, as well as ammonia (used as a standard) were investigated. Ammonia which was used in a concentration of four times that of any other amine was a poor catalyst. The time required for reaction was 12.5 hours, but a yield of only 59 per cent TMP was obtained. The TMP was contaminated with chloreton and the rest of the reaction mixture was composed mostly of chloreton. This failure may have been a solubility factor as ammonia contains no organic solublizing groups, and the salt formed was insoluble in the reaction mixture.

Tetraethylammonium iodide did not give the expected TMP but instead gave exclusively allyl-TMP in 88 per cent yield. It was, however, a catalyst in that the time required for the reaction to

go to completion was the same as with other amines. This unexpected result is easily understood when the salt is considered. It was observed that thionyl chloride reacted immediately with the salt, liberating iodine, and the iodine caused rearrangement of TMP to allyl-TMP. The basis for this statement can be shown by considering the results obtained from tetramethylammonium chloride.

The catalytic ability of quaternary salts was shown quite vividly with tetramethylammonium chloride. The salt was dissolved in 20 ml. thionyl chloride and added to the refluxing chlorotone-thionyl chloride mixture. In the 25 minutes the mixture had been refluxing without catalyst only 0.2 equivalents of gas had been liberated yet in the four minutes it took to add the catalyst 0.37 equivalent of gas was liberated. The yield of TMP from this catalyst was comparable to those obtained using other amines or salts. A consideration of the type of entities that catalyze this dehydration show a somewhat common structure, this being R_3NR' . The R is alkyl or hydrogen. R_3 can be a mixture of organic residues and hydrogen, but at least one R must be an organic solubilizing group for the medium with chlorotone as used. The other type of ion species that could possibly be catalytic would be Cl^- . The relationship of these two ions is such that the Cl^- ion could hardly catalyze the TMP formation.

Ikenberry showed that chloride ion in the form $FeCl_4^-$ or other Lewis acids gave exclusively 1,1,1,2-tetrachloro-2-methylpropane in this reaction. In order to fully explain the role of the catalyst, kinetic studies would have to be carried out, but this was beyond the scope of the present work.

By use of alcohols that have groups having an inductive effect equal to or greater than that of the trichloromethyl, it may be possible that dehydration could be carried out using addition of amines for catalysis with thionyl chloride. This line of activity is indicated as a type reaction.

Effect of Impurities on the Dehydration of Chloretone

A test of this effect was carried out for several purposes. Pledger (12) found that concentration 0.1 mole per cent of Lewis acids would cause rearrangement of TMP to allyl-TMP. In the reaction of thionyl chloride and chloretone Ikenberry (6) showed that one mole per cent of aluminum chloride catalyzed the corresponding chloride formation. Both of these concentrations are greater than those of Lewis acid impurities in technical refined grades of thionyl chloride. A concentration of 0.2 mole per cent of ferric chloride and aluminum chloride was added to the thionyl chloride. This concentration is greater than that present in the technical grade of thionyl chloride.

It is well known that such metal halides are deactivated as catalysts in the Friedel-Crafts reaction by amines, probably by complex formation. Therefore pyridine would be expected to overcome the effects of the metal salts in the present case. When added in a concentration six times that of the metal salts present, the desired result was obtained. The mixture acted in the same manner as when the Lewis acids were not added and only amine had been added.

The yield of TMP from such a procedure was 73 per cent while

that of allyl-TMP was nine per cent. The over-all yield was practically the same as in the controls. The fact that the Lewis acids known to be present initially did not cause any significant yield of allyl-TMP gives considerable support to the point that part of the action of the amines was that of a complexing agent. By this complexing the Lewis acids were inactivated. None of the tetrachloromethylpropane was detectable, which also supports this point.

Synthesis of the Chlorosulfinic Ester of Chloretone

It has been pointed out that addition of an amine catalyzes the thionyl chloride dehydration of chloretone to TMP. However, it was unknown which step in the dehydration was catalyzed most. Furthermore, the rate controlling step was unknown. The best method for determining these unknowns would be to isolate the postulated chlorosulfinic ester.

Following the procedure of Pledger (12) using amine, carbon tetrachloride and two moles of thionyl chloride the chlorosulfinic ester was formed in almost quantitative yield in one hour. Gerrard (2) had prepared chlorosulfinic esters of primary alcohols using one mole equivalent of tertiary amine. He found that the hydrochloride of tertiary amines in low concentrations catalyzed the decomposition of these esters to the corresponding chlorides. In no case did he get olefins or hydrogen chloride evolution.

A control experiment without amine run at the same time required eight hours to go to completion. The product from this

was of inferior quality and appeared to contain an appreciable amount of TMP absorbed on the crystals. The TMP and chlorosulfinic ester could not be separated because of the instability of the ester. The formation of TMP in this case was assessed to the long reaction time in the presence of thionyl chloride, a circumstance observed previously by Lewis and Boozer (9). The chlorosulfinic ester was soluble in all solvents, both polar and non-polar. It changed to chlorethane from the action of moist air. By rapidly weighing the needles of the ester, dissolving them in anhydrous ethanol and rapid titration with sodium hydroxide a value of 257 was obtained for the observed hydrogen chlorine liberated by the ethanolysis. The calculated value for this corresponds to 260.

Thermal Decomposition of the Chlorosulfinic Ester
of Chlorethane to TMP

No Solvent. As was expected the decomposition of the chlorosulfinic ester was the slow step and hence the rate controlling step. A thermal decomposition method without solvent was chosen for two purposes: (a) any solvent effect would be eliminated, and (b) the chlorosulfinic ester could possibly go through a mechanism to give either olefin or chloride production.

Without a catalyst and at 80° C the decomposition took 23 hours to go to completion. The products obtained were exclusively TMP and allyl-TMP, in yields of 80 and nine per cent conversion, respectively. No corresponding chloride was isolated.

Since the intermediate was isolated, the path of the reaction

values, but they can be used to some degree in a qualitative comparison.

In the same length of reaction time the catalyst-containing mixture liberated 1.24 equivalents of acidic gas while the control liberated only 0.96 equivalent. This difference, 0.28 equivalents, together with the reaction time of seven hours indicates that while the solvent effects of thionyl chloride are the more important, the presence of the amine catalyst does aid in the decomposition to a lesser degree.

Lewis and Boozer (9) have studied the thermal decomposition of chlorosulfinic esters of secondary alkyl alcohols in the polar solvent dioxane and non-polar solvent 2,2,4-trimethyl-pentane. They report the decomposition was a first-order reaction yielding olefin and alkyl chloride as the principal product when dioxane was used as solvent. These authors found that 2-butyl chlorosulfite, when decomposed in dioxane at 100° C, gave a 60 per cent conversion to the olefin. In the non-polar solvent first order kinetics was observed, but the rate of decomposition was much slower.

As the inductive effect of the three chlorines tends to stabilize the chlorosulfinic ester of chloretone and causes it to be different from an ordinary tertiary alkyl chlorosulfinic ester, an analogy can be drawn with the secondary-alkylchlorosulfinate. The slow rate of decomposition in the non-polar solvent found by these authors would be analogous to the stability of chloretone chlorosulfinate in carbon tetrachloride and explain the reason that the chlorosulfinate could be isolated when

this or a similar solvent was used. In a like manner the ease of decomposition of the chlorosulfinic ester in thionyl chloride would be explained, since thionyl chloride would be a more polar solvent than dioxane.

Syntheses of Diethyl Dichloromethylallylmalonates

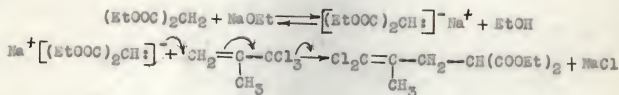
A search of the literature showed that no work has been carried out on the synthesis of these compounds. Such compounds as these could be of importance as intermediates in the synthesis of barbiturates.

de la Mare (1) has recently studied the reaction of TMP and the nucleophilic thiophenoxide anion. He describes the reaction as being of the S_N2' type. As malonic esters readily form a nucleophilic carbanion under the influence of sodium ethoxide it was of interest to compare reactions and products of malonate carbanions with TMP.

Synthesis of Diethyl 3,3-Dichloro-2-methylallylmalonate (I) Using TMP. The indicated product was synthesized in a conversion yield of 53 per cent. A side reaction, which is quite common in alkylation of malonic esters, gave a yield of 20 per cent of the disubstituted ester, diethyl bis(3,3-dichloro-2-methylallyl) malonate (II). I is a liquid, b.p. 95°C (0.2 mm), R.I. 1.4678, D. 1.182; while II is a solid, m.p. $66-67^\circ\text{C}$. These properties simplified separation difficulties often found in this type of synthesis.

Infrared analysis by A. W. Baker of the Dow Chemical Company indicated that both I and II contained the $\text{Cl}_2\text{C}=\text{C}(\text{CH}_3)-$ group

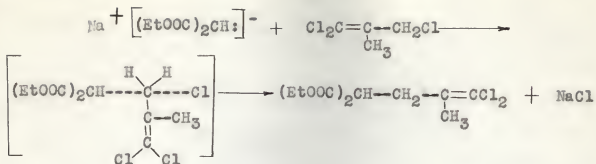
(6.16 and 11.1-11.2 microns) and ester group (5.71-5.77 microns). From the above considerations the course of reaction can be most conveniently represented by the following general equation:



It can be seen that the equation given above is the $\text{S}_{\text{N}}2'$ type of displacement. Since the reaction was carried out in anhydrous alcohol a preliminary rearrangement of the halide is unlikely. Another method of forming such a product would be the formation of the normal O-alkylated derivative followed by a Claisen type rearrangement. This, however, seems unlikely as no other products are detectable in the reaction mixture. The $\text{S}_{\text{N}}2'$ type would be greater enhanced by the three chlorine atoms in TMP, not only as a local effect but also to assist by shifting the screen of the unsaturation electrons away from the carbon atom being attacked.

Using Allyl-TMP. The products obtained by this procedure were the same as those obtained from TMP. Comparison of yields between the two procedures showed that from allyl-TMP a conversion yield of 63 per cent of (I) was obtained which was somewhat higher than that realized from TMP. Correspondingly the yield (eight per cent) of (II) was lower. This was probably due to the fact that the ester was added in excess in this reaction.

The course of the reaction can be expressed by the following equation:



The product from this reaction fits in nicely according to theory. It is of the $\text{S}_{\text{N}}2$ type of displacement. At the attack of the negatively charged ion, a polarization of the double bond would be produced which would facilitate the approach of the ion. The vinyl chloride grouping present should enhance this effect.

One-Step Synthesis of Diethyl Bis(3,3-dichloro-2-methylallyl) malonate (II). As significant yields of this product were formed in the synthesis of the monosubstituted ester, it was desired to prepare II as dominant product in one step. Such a method would have a definite advantage over a two-step process, provided that undesirable side reactions did not occur. Using a molar ratio of 2:1:2 between sodium, ester, and halide respectively, yields of 71 per cent from TMP and 76 per cent from allyl-TMP of II were isolated. A reaction time of 18 hours was chosen arbitrarily. A shorter reaction time would probably have been as effective.

The reaction was visualized as proceeding according to the following: equilibrium was quickly established between sodium ethoxide and ester to give the mono sodio derivative which in turn reacted with TMP to give the monosubstituted ester; then the whole cycle repeated for putting on the second dichloro-methylallyl group. This whole process would have to be rapid, and the addition

of TMP slow to prevent dichloromethylallyl ethyl ether formation.

A two-step process, rather than formation of the disodio salt, would be in agreement with fact that sodium of the mono sodio salt would tend to make the second hydrogen less acidic. This decrease in acidity would make removal of the second hydrogen, in one step, less probable.

Synthesis of Diethyl Methyl-(3,3-dichloro-2-methylallyl)-malonate (III). This synthesis was carried out by reacting TMP and diethyl methylmalonate. This compound was not reported in the literature. Yields, however, were not so high as expected. The product III isolated in 63 per cent conversion had the following physical properties, b.p. 96° (0.3mm) - 110° C (1.1 mm), R.I. 1.4675, D 1.160.

The isolated compound III was somewhat impure. The residue solidified and recrystallization gave a product which showed no depression of m.p. when mixed with bis(3,3-dichloro-2-methylallyl) malonate (II). This component was due to the small amount of diethyl malonate in the supplied supposedly pure white label grade of diethyl methylmalonate. Since the II was found, then the sought product, diethyl (3,3-dichloro-2-methylallyl) methyl malonate (III) must have contained a small amount of diethyl 3,3-dichloro-2-methylallylmalonate (I). Since diethyl malonate cannot be separated by distillation from diethyl methylmalonate, then III and I are naturally also present in the sought product in the same ratios as were said two malonic esters in the starting material.

It was of interest to compare the action of bromine in

carbontetrachloride on both the non-methylated dichloromethylallylated product (I) and on the methylated dichloromethylallylated product (III). The monosubstituted ester (I) immediately liberated hydrogen bromide while with III there was no change in the bromine color. Since monosubstituted malonates are known to give this test while disubstituted do not, evidently III was the desired diethyl methyl-(3,3-dichloro-2-methylallyl)-malonate.

Synthesis of Ethyl 3,3-Dichloro-2-methylallylacetate (IV)

The reaction of TMP with acetoacetic ester in the presence of sodium ethoxide and ethanol was found to be unusual. From work-up and distillation there were obtained 30 per cent by weight of forerun and a 51.5 per cent yield of a product that had b.p. 72.5° (0.8 mm) - 91° (2.1 mm) R.I. 1.4705-1.4716, D. 1.167.

The molecular refraction and chemical analysis, of a heart cut, however, did not check for a substituted acetoacetic ester. Infrared studies by A. W. Baker of The Dow Chemical Company indicated that the compound contained a $\text{Cl}_2\text{C}=\text{C}-(\text{CH}_3)$ group (11.13, 6.15 microns) and an ester carbonyl at 5.76 microns, but no ketone carbonyl band. Also the characteristic acetoacetic ester chelate band (15) near 6.0 microns was not found. Recalculation of the molecular refraction and chemical analysis checked for ethyl 3,3-dichloro-2-methylallylacetate (IV), the deacetylated product from that originally expected. The calculated identifying values for IV check with those observed (see Experimental).

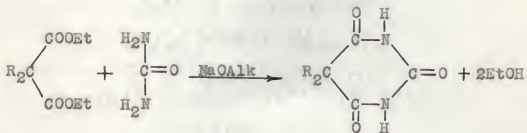
The ester IV was recently reported by Kundiger and Richardson

in the cold quickly, and it was immediately ether extracted and dried.

The three per cent yield of a product in the residue that gave ultimate elementary analyses corresponding to ethyl alpha, alpha (3,3-dichloro-2-methylallyl)acetoacetate (V) in the same reaction is hard to explain. It is valuable in showing that three per cent (or possibly more under different conditions), of the disubstituted acetoacetic ester can be obtained without deacetylation.

Syntheses of 5-(3,3-Dichloro-2-methylallyl)-5-Substituted-Barbituric Acids

One of the type reactions of substituted malonic esters is the condensation with urea in the presence of alkali metal alkoxide to form the corresponding substituted barbituric acid, represented by the following general equation:



These barbiturates are of value as drugs as they often have the ability to act as sedatives and hypnotics. Barbiturates with a $\text{Cl}_2\text{C}=\text{C}$ type grouping have not been prepared previously so it should be of interest to compare their physiological properties with known varieties of substituted barbiturates.

The three different dichloromethylallylated malonic esters

were subjected to this condensation. The corresponding barbiturates were isolated in yields of 11 to 58 per cent conversion. It was of interest to note the stability of the vinyl chlorides in these syntheses. Even under the strong basic conditions used, these chlorides were resistant to attack and the original configuration was retained.

The 5-(3,3-dichloro-2-methylallyl)barbituric acid (VI) was prepared in 46 per cent conversion yield and in 52 per cent recovery yield by a reaction time of 5.5 hours. The analytically pure product has a melting point of 229-231° C. This compound is appreciably soluble in water.

The 5,5-(3,3-dichloro-2-methylallyl)barbituric acid (VII) however, was prepared in a much lower yield. From a 35.5 hour reaction time, an 11 per cent conversion yield of VII was obtained. As 76 per cent of the starting ester was recovered, the recovery yield figures to 46 per cent. The pure product has m.p. 194-195° C. It could be that the lower yield of VII was due in part to the greater amount of solvent used in this preparation. A consideration of the nature of the starting ester, however, indicates low yields. Construction of the molecular model beforehand showed that the barbiturate could be formed, but its formation is sterically hindered and thus very slow and difficult. To cause the reaction to proceed would probably require a higher boiling solvent. In one reaction not reported in detail, the use of the stronger base potassium tertiary butoxide in the corresponding alcohol resulted only in the decomposition of the starting ester.

The 5-methyl-5-(3,3-dichloro-2-methylallyl)barbituric acid (VIII) was prepared under somewhat different reaction conditions. Sodium methoxide was used as a condensing agent and secondary-amyl alcohol was used as a solvent.

This barbiturate was prepared in 58 per cent conversion yield using a reaction time of 24 hours. This yield was somewhat higher than in the preceding case of the 46 per cent yield. Probably part of the explanation of the low yields is due to solubility losses and manner of work-up. These barbiturates exhibit a great tendency to occlude starting ester on the crystal surface. In the case of VIII it was necessary to use a modified vacuum sublimation method to remove completely the occluded starting material. It was felt that this was the reason for the difficulty in some cases in getting very close checks in the ultimate analyses.

On the whole, if these barbiturates exhibit no adverse toxicological effects and if they do have hypnotic and sedative properties, a route to syntheses of a vast number of new derivatives is opened. The biological activity tests will be carried out in the laboratories of The Dow Chemical Company.

SUMMARY

This investigation has shown that 1,1,1-trichloro-2-methyl-2-propanol can be successfully dehydrated by thionyl chloride to 3,3,3-trichloro-2-methyl-1-propene when a variety of amines and amine salts are added in small amounts to the reaction mixture. These amines and salts behave as catalysts, and shorten the time

necessary for completion of the reaction from 30 hours to 5.5 to 10 hours. It also has been shown that the catalysts inactivate the Lewis acids that otherwise produce undesirable side reactions during the desired dehydration.

This study has further shown that the postulated intermediate, the chlorosulfinic ester, can be isolated. The ester can be thermally decomposed both with or without solvent to the desired olefin.

The olefin, 3,3,3-trichloro-2-methyl-1-propene or its allylic isomer 1,1,3-trichloro-2-methyl-1-propene were shown to react with diethyl malonate in the presence of sodium ethoxide to form either the mono or bis dichloromethylallylated malonic ester to the greater extent, depending on the control of the reaction conditions.

Acetoacetic ester in the same type of reaction does not give the expected substituted acetoacetate, but instead is deacetylated to give 3,3-dichloro-2-methylallylacetate.

The new dichloromethylallylated malonic esters condensed with urea, using a sodium alkoxide and gave the corresponding barbiturates in 11 to 58 per cent conversion yield.

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation for the guiding influence and suggestions of Dr. Donald G. Kundiger under whose direction this work was done. The author also wishes to thank The Dow Chemical Company for a research grant which supported this work, Kansas State College for the use of its facilities, and the faculty of the Department of Chemistry for their generous advice and encouragement.

The author is further indebted to Dr. A. W. Baker of The Dow Chemical Company and Mr. William G. Fately of the Department of Chemistry, Kansas State College, for their assistance in making infrared analyses, and to The Dow Chemical Company for the quantitative analyses reported herein.

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SYNTHESIS AND REACTIONS OF 3,3,3-TRICHLORO-2-METHYL-1-PROPENE
AND OF 1,1,3-TRICHLORO-2-METHYL-1-PROPENE

by

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B. S., Kansas State College of
Agriculture and Applied Science, 1954

AN ABSTRACT OF A THESIS

submitted in partial fulfillment of the

requirements for the degree

MASTER OF SCIENCE

Department of Chemistry

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

1955

In the dehydration of 1,1,1-trichloro-2-methyl-2-propanol with thionyl chloride to give 3,3,3-trichloro-2-methyl-1-propene by the addition of amines to form catalysts, conversions of 55 to 83 per cent were obtained in all except one case. A variety of amines were added and their hydrochloride salts formed from this reaction in situ. A typical quaternary ammonium chloride was also effective. The catalytic amounts were tested for the following amines: aniline, aniline hydrochloride (put in as such), mono-*t*-butylamine, mono-*t*-octylamine, di-*n*-butylamine, piperidine, pyridine, *N,N*-dimethylaniline, triethylamine, and quinoline. The following quaternary compounds: tetraethylammonium iodide and tetramethylammonium chloride, as well as ammonia, were tested for comparison.

One dehydration in which known quantities of Lewis acids were added to the thionyl chloride was carried out. These Lewis acids, which had been shown previously to be catalytic in forming 1,1,1,2-tetrachloro-2-methylpropane in the reaction of chlorethane with thionyl chloride and to cause rearrangement of TMP to allyl-TMP, were rendered ineffective by the addition of an amine to the reaction mixture.

The chlorosulfinic ester of 1,1,1-trichloro-2-methyl-2-propanol was synthesized in 98 per cent yield to prove its intermediate existence in the thionyl chloride dehydration. This chlorosulfinic ester was converted to 3,3,3-trichloro-2-methyl-1-propene by the action of heat alone in 79 per cent yield.

Three new diethyl 3,3-dichloro-2-methylallyl-substituted-malonates were synthesized. They were: the mono-dichloromethyl-

allyl"; bis-dichloromethylallyl"; and dichloromethylallyl-methylmalonates.

An attempted synthesis of ethyl alpha-(3,3-dichloro-2-methylallyl)acetoacetate gave a 61 per cent yield of ethyl 3,3-dichloro-2-methylallylacetate in one step.

The corresponding substituted barbituric acids were prepared from the new substituted malonic esters. The conversion yields isolated were: 5-(dichloromethylallyl), 46 per cent; 5,5-(dichloromethylallyl), 11 per cent; 5-methyl-5-(dichloromethylallyl), 58 per cent.

