ml. of water and almost enough silver nitrate, then rapidly titrated to the coagulation end-point.

Table III gives second-order rate constants calculated from initial slopes (not over 60% reaction) since curvature appeared later in the runs with high concentration of acetate ion due to competition by acetate ion for the epichlorohydrin. The increased rate with the highest concentration of buffer must be due to a medium effect on equilibrium or rate constants, rather than to general acid catalysis.

CAMBRIDGE 39, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, KANSAS STATE COLLEGE]

The Preparation and Reactions of 3,3-Dichloro-2-methylpropenal

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The preparation of 3,3-dichloro-2-methylpropenal by oxidation of the corresponding alcohol is described. This aldehyde undergoes normal reactions with carbonyl reagents but gives interesting and unexpected reactions with piperidine and with chlorobenzene in the presence of sulfuric acid.

The chemistry of β,β-dichloro-α-substituted acroleins has received very limited study. Previous work has been concerned primarily with the synthesis of β,β-dichloroacrolein[1] and α-(p-tolyl)-β,β-dichloroacrolein.[2] The methods for obtaining these two aldehydes, however, differ essentially from the methods used in the present work, which was initiated as a study of the reactivity of the chlorine substituents in such a conjugated system as 3,3-dichloro-2-methyl-2-propenal (II). This unsaturated aldehyde was prepared in good yields (54–60%) by the oxidation of the corresponding alcohol I with either nitric or chromic acids. The stability of the aldehyde to further oxidation by these reagents is remarkable. The route used for the preparation of II is

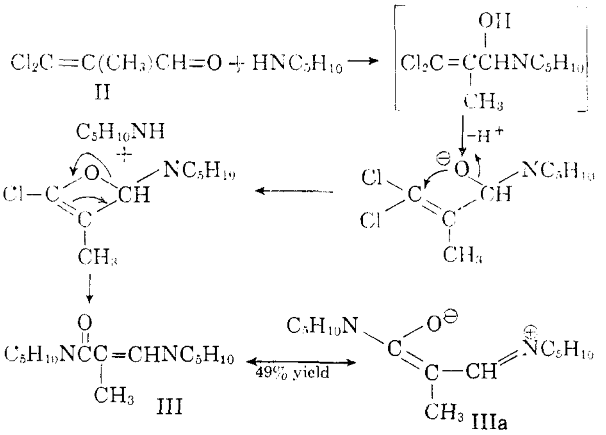
$$Cl_3CC(OH)(CH_3)_2 \xrightarrow[\text{quinoline}]{SOCl_2}$$
$$Cl_3CC(CH_3){=}CH_2 \xrightarrow{2\ N\ NaOH}$$
$$\underset{I}{Cl_2C{=}C(CH_3)CH_2OH} \xrightarrow[\text{or}\ H_2Cr_2O_7]{HNO_3} \underset{II}{Cl_2C{=}C(CH_3)CHO}$$

There were trace amounts of nitrogenous impurities in the distilled samples of II when nitric acid was used in the oxidation. When chromic acid was used, a small amount (8–10%) of the aldehyde II was converted to the acetal $Cl_2C{=}C(CH_3)CH(OCH_2C(CH_3){=}CCl_2)_2$ by reaction with the alcohol I.

The literature contains no examples of formation of aliphatic aldehydes from the use of nitric acid on alcohols. Helferich, *et al.*,[3] have reported the oxidation of *o*- and *p*-nitrobenzyl alcohol to the corresponding aldehydes by this reagent.

Compound II gave normal derivatives with hydroxylamine and with *p*-nitro- and 2,4-dinitrophenylhydrazine and formed acetals and thioacetals readily.

Direct reaction of a large molar excess of piperidine with the aldehyde II gave in addition to the theoretical amount of piperidine hydrochloride 1-(2-methyl-3-(1-piperidyl)-propenoyl)-piperidine (III) in 49% yield.



Its structural assignment is based on its composition, its molecular weight and its hydrolysis with dilute sodium hydroxide to two equivalents of piperidine and an amorphous waxy white solid, probably an aldol polymer of propionaldehyde, derived from the primary hydrolysis product $HOOCCH(CH_3)CHO$ by decarboxylation and polymerization. Presumably the dipolar structure IIIa makes a substantial contribution to the structure of III, since its water solubility is unusually high (about 9%) and its infrared carbonyl stretching frequency occurs at 6.22 μ. The structure $\overset{-N-}{\overset{|\quad\ |}{RCOC{=}C-}}$ is known[4] to cause a shift in the carbonyl frequency of 20–80 cm.$^{-1}$, attributed to the contribution of an ionic resonance form analogous to IIIa. The shift of the carbonyl frequency for the amide structure of III in our case is a shift of 22–62 cm.$^{-1}$ and thus is in qualitative agreement with the results observed for β-amino-α,β-unsaturated ketones.[4,5] In the case at hand, the contribution of IIIa should be somewhat less than that of the dipolar forms of β-amino-α,β-

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(1) (a) E. Levas and E. Levas, *Compt. rend.*, **232**, 521 (1951); (b) E. Levas and E. Levas, *ibid.*, **230**, 1669 (1950); (c) M. Levas, *Ann. chim.*, **7**, 697 (1952); (d) M. S. Kharasch, Otto Reinmuth and W. H. Urry, THIS JOURNAL, **69**, 1105 (1947); (e) A. N. Nesmeyanov, R. Kh. Freidlina and L. I. Zakharkin, *Doklady Akad. Nauk S.S.S.R.*, **97**, 91 (1954); (f) **99**, 781 (1954).

(2) R. L. Tse and M. S. Newman, *J. Org. Chem.*, **21**, 638 (1956).

(3) B. Helferich, R. Streeck and E. Günther, *J. prakt. Chem.*, **151**, 251 (1938); *C. A.*, **33**, 1689 (1939).

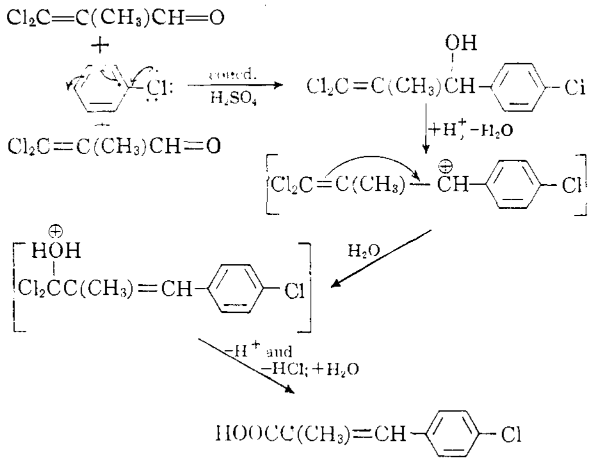
(4) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1956, Ch. 9, pp. 125–126.

(5) N. H. Cromwell, F. A. Miller, A. R. Johnson, R. L. Frank and D. J. Wallace, THIS JOURNAL, **71**, 3337 (1949).

unsaturated ketones. The carbonyl absorption of the substance, 6.22 μ, is thus considered to be compatible with structure III.

Attempts to isolate the product of the reaction of II and di-*n*-butylamine were unsuccessful, although the theoretical amount of di-*n*-butylamine hydrochloride was isolated. An oil was obtained which decomposed upon attempted distillation.

An unusual reaction took place when the aldehyde II was treated with a mixture of chlorobenzene and concentrated sulfuric acid. The product formed was *trans*-3-(*p*-chlorophenyl)-2-methyl-2-propenoic acid (IV), identical with the acid obtained from the Perkin reaction of *p*-chlorobenzaldehyde with propionic anhydride in the presence of sodium propionate. The formation of IV from II can be rationalized as



IV

We discovered that 1,1,3-trichloro-2-methyl-1-propene can be hydrolyzed directly in 78% yield with boiling 2 *N* sodium hydroxide to 3,3-dichloro-2-methyl-2-propen-1-ol. The unrearranged 3,3,3-trichloro-2-methyl-1-propene can also be hydrolyzed with dilute sodium hydroxide to I in 69% yield, and thus any mixture of the two trichloro isomers can be hydrolyzed successfully to the 3,3-dichloro-2-methyl-2-propen-1-ol.

Experimental[6]

3,3-Dichloro-2-methyl-2-propen-1-ol (I) by Direct Hydrolysis.—A mixture of 810 g. (5.1 moles) of 1,1,3-trichloro-2-methyl-1-propene[7] and 212 g. (5.3 moles) of sodium hydroxide in 2500 ml. of water was stirred at high speed at reflux for 8 hours. This amount of time was found to be the minimum necessary for the neutralization of the sodium hydroxide. Cooling the product to room temperature, separation of the organic layer, and drying over magnesium sulfate afforded 670 g. of a brown viscous oil. Distillation of this oil at reduced pressure yielded 550 g. (78.4%) of 3,3-dichloro-2-methyl-2-propen-1-ol (I), b.p. 91–92° (16 mm.), n^{20}_{D} 1.4998, and 96.5 g. (7.3%) of bis-(3,3-dichloro-2-methyl-2-propen)-ether, b.p. 77–78° (0.17 mm.), n^{20}_{D} 1.5116–1.5120, for a total conversion of 93%.

3,3-Dichloro-2-methyl-2-propenol (I) by Hydrolysis of 3,3,3-Trichloro-2-methyl-1-propene.—A stirred mixture containing 160 g. (1.0 mole) of 3,3,3-trichloro-2-methyl-1-propene and 40 g. (1.0 mole) of sodium hydroxide in 500 ml. of water was heated to reflux for 38 hours, the time necessary for neutralization of the sodium hydroxide. Separation of the organic layer after cooling, drying with sodium sulfate and distillation yielded 97 g. (69%) of 3,3-dichloro-2-methyl-2-propenol (I), b.p. 83–85° at 12 mm., n^{20}_{D} 1.4995, and 13.2 g. (5%) of the bis-ether, b.p. 138–141° at 12 mm., n^{20}_{D} 1.5120.

3,3-Dichloro-2-methyl-2-propenal (II) by Nitric Acid Oxidation of 3,3-Dichloro-2-methyl-2-propenol (I).—3,3-Dichloro-2-methyl-2-propenol (I, 141 g., 1.0 mole) was added dropwise over a 2-hour period to a stirred amount of 130 g. (2.0 moles) of concentrated nitric acid cooled to −3°. The temperature was maintained at 0–10° for one hour after addition, then allowed to warm to room temperature and stand overnight. During the addition, brown fumes were evolved continuously from the solution and it remained a brownish-green in color. After removal of these gases by bubbling nitrogen through the solution, it took on a soft blue appearance. Separation of the organic layer and repeated washings with 25-ml. portions of 10% sodium bicarbonate left a yellow oil which was dried over magnesium sulfate and distilled to yield 85 g. (60%) of 3,3-dichloro-2-methyl-2-propenal (II), b.p. 47–49° at 15 mm., n^{20}_{D} 1.5052–1.5056. Twenty grams of a white solid residue remained in the distilling flask. This residue contained nitrogen, but attempts to isolate any single component were unsuccessful.

Anal. Calcd. for $C_4H_4Cl_2O$ (II): C, 34.54; H, 2.88. Found: C, 34.04; H, 2.86.

A nitrogen-containing impurity was present in II prepared in this manner and attempts to remove it were unsuccessful. However, it did not influence the preparation of derivatives as they were equally well prepared from aldehyde II obtained by nitric acid oxidation or from II obtained by chromic acid oxidation.

3,3-Dichloro-2-methyl-2-propenal (II) from Dichromate–Sulfuric Acid Oxidation of I.—One mole (141 g.) of 3,3-dichloro-2-methyl-2-propen-1-ol was heated to 57° under a pressure of 30 mm. and a solution of 84 g. (0.35 mole) of ammonium dichromate and 134 g. (1.35 moles) of concentrated sulfuric acid in 400 ml. of water was added dropwise with rapid stirring. The resulting steam distillation removed the aldehyde as it formed and it was condensed into a flask immersed in ice. After the addition was complete, the solution was heated to 80° for 10 minutes. The distillate was separated and the water layer extracted with two 25-ml. portions of carbon tetrachloride, which were combined with the organic fraction. The combined extracts were dried over magnesium sulfate and distilled to yield 74.8 g. (54%) of 3,3-dichloro-2-methyl-2-propenal (II), b.p. 65–66° (50 mm.), n^{20}_{D} 1.5045, and 31.0 g. (8%) of the acetal of the aldehyde, *viz.*, bis-(3′,3′-dichloro-2′-methyl-2′-propenoxy)-1,1-dichloro-2-methyl-1-propene, b.p. 122–123° at 0.015 mm., n^{20}_{D} 1.5226. The reaction also can be carried out at atmospheric pressure and 140°, yield 41% of II.

Anal. Calcd. for $C_4H_4Cl_2O$ (II): C, 34.54; H, 2.88; Cl, 51.01. Found: C, 34.00; H, 2.93; Cl, 50.51. For the acetal of I and II: Calcd. for $C_{12}H_{14}Cl_6O_2$: C, 35.80; H, 3.50; Cl, 52.85. Found: C, 35.84; H, 3.56; Cl, 50.32.

Aldehyde II was characterized by formation of these derivatives:

The 2,4-dinitrophenyl hydrazone was recrystallized three times from 95% ethanol and was obtained as orange needles, m.p. 194.5–195°. *Anal.* Calcd. for $C_{10}H_8Cl_2N_4O_4$: Cl, 22.18; N, 17.56. Found: Cl, 22.03; N, 16.84.

The *p*-nitrophenyl hydrazone was obtained as yellow-orange needles by recrystallization twice from a 5:2 mixture of absolute ethanol–carbon tetrachloride, m.p. 228–229° dec. *Anal.* Calcd. for $C_{10}H_9Cl_2N_3O_2$: Cl, 25.82; N, 15.33. Found: Cl, 25.85; N, 14.79.

The acetal, 3,3-bis-(3′,3′-dichloro-2′-methyl-2′-propenoxy)-1,1-dichloro-2-methyl-1-propene, was characterized by hydrolysis with 5% hydrochloric acid and preparation of the 2,4-dinitrophenyl hydrazone, m.p. 194.5–195° (no depression when admixed with the 2,4-dinitrophenylhydrazone of the parent aldehyde II).

1-(2-Methyl-3-(1-piperidyl)-propenoyl)-piperidine (III) from Reaction of 3,3-Dichloro-2-methyl-2-propenal and Piperidine.—To a stirred solution of 23.8 g. (0.28 mole) of piperidine in 200 ml. of anhydrous ether cooled in an ice-bath, 5.6 g. (0.04 mole) of 3,3-dichloro-2-methyl-2-propenal in 100 ml. of anhydrous ether was added dropwise over a period of one hour. The solution was allowed to stand for 48 hours with the contents warming to room temperature and the formation of a copious precipitate of piperi-

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[6] Melting points and boiling points are uncorrected.

[7] D. G. Kundiger, Huey Pledger and L. E. Ott, THIS JOURNAL, **77**, 6659 (1955).

dine hydrochloride. The solution was stirred vigorously, then filtered to yield 9.7 g. (100%) of piperidine hydrochloride. The ether was removed, 100 ml. of purified ligroin (b.p. 70°) was added, and the resulting solution was cooled to room temperature. The resulting pale yellow solid (4.82 g.), **1-(2-methyl-3-(1-piperidyl)-propenoyl)-piperidine** (**III**), was extracted in a Soxhlet extractor, using purified ligroin (b.p. 70°) as solvent. The ether solution was treated with Norite, concentrated, and the resulting solid was recrystallized twice from ligroin (70°). Further recrystallization of this solid (4.6 g., 49% yield) did not change the melting point (129–131°) of III. Its infrared spectrum in Nujol mull showed strong bands at 3.45, 3.55, 6.2, 6.55, 7.0, 7.7, 9.77 and 10.86 μ, plus a number of bands characteristic of the spectrum of piperidine. No N–H or –O–H bands were present. At 25°, 6.82 ml. of water is required to dissolve 0.6097 g. of III, corresponding to a solubility of 9 g. per 100 cc. of water.

Anal. Calcd. for $C_{14}H_{24}N_2O$: C, 71.19; H, 10.26; N, 11.86; mol. wt., 236. Found: C, 71.16; H, 10.31; N, 11.51; mol. wt., 245, 234 (Rast method).

1-(2-Methyl-3-(1-piperidyl)-propenoyl)-piperidine (III) or Piperidyl-3-(N-piperidyl)-2-methyl-2-propenamide and 3% Sodium Hydroxide.—Treatment of 0.3624 g. (1.53 mmoles) of the above amide with 15 ml. of 3% sodium hydroxide solution for 24 hours at 92° resulted in hydrolysis to piperidine and a waxy substance that appeared polymeric and was found intractable. The piperidine was distilled into a receiver containing 10 ml. of 10% hydrochloric acid. Evaporation resulted in 0.3345 g. (2.78 mmoles, 91% of two equivalents) of piperidine hydrochloride, m.p. 240–242°; mixture melting point with authentic sample was not depressed.

3,3-Dichloro-2-methyl-2-propenal (II) with Di-*n*-butylamine.—A mixture of 5.6 g. (0.04 mole) of 3,3-dichloro-2-methyl-2-propenal (II), 36.2 g. (0.28 mole) of di-*n*-butylamine and 100 ml. of anhydrous diethyl ether was allowed to stand at room temperature for 4 days. The solution was filtered and 12.1 g. (93%) of di-*n*-butylamine hydrochloride, m.p. 284–286°, no depression of m.p. on admixture with an authentic sample, was obtained. Removal of the excess di-*n*-butylamine was accomplished under reduced pressure and left a dark viscous oil containing a small quantity of the hydrochloride. This oil was washed with water, with sodium bicarbonate solution, with water, and then taken up in ligroin and dried over magnesium sulfate. Attempted crystallizations did not succeed, so distillation at 0.05 mm. was attempted. The mixture decomposed to black tar. No material would steam distil out of this tar.

3-(*p*-Chlorophenyl)-2-methylpropenoic Acid (IV).—To a well stirred solution of 14 g. (0.10 mole) of 3,3-dichloro-2-methylpropenal in 14 g. (0.13 mole) of chlorobenzene, 25 g. (0.25 mole) of concd. sulfuric acid was added over a period of one hour at room temperature. The mixture was stirred vigorously for 16 hours and then was heated to 80° for 24 hours. During this latter time one equivalent (titration) of hydrogen chloride was liberated. The solution was cooled to room temperature and poured over 100 g. of cracked ice; 3 g. (15%), m.p. 167–169°, of **3-(*p*-chlorophenyl)-2-methyl-2-propenoic acid** was obtained by filtration. Steam distillation of the filtrate to remove excess chlorobenzene left a dark brown crystalline residue which was taken up in ethanol, Norited and crystallized twice from 95% ethanol to yield an additional 5 g. (25%) of the same acid, as fine white needles, m.p. 168–169°. No other organic products were obtained.

Anal. Calcd. for $C_{10}H_9ClO_2$: C, 61.05; H, 4.58; Cl, 18.07; neut. equiv., 196.5. Found: C, 60.67; H, 4.54; Cl, 18.16; neut. equiv., 197.

Oxidation of 0.1970 g. (1.0 mmole) of the acid with 1.105 g. (7.0 mmoles) of potassium permanganate in 25 ml. of water at room temperature, destruction of excess permanganate with sodium bisulfite and acidification with sulfuric acid precipitated 0.141 g. of *p*-chlorobenzoic acid, m.p. 245–246°; admixture with authentic sample of *p*-chlorobenzoic acid gave no depression.

***trans*-3-(*p*-Chlorophenyl)-2-methyl-2-propenoic Acid (IV) by Perkin Synthesis.**—A mixture of 7.5 g. (0.053 mole) of *p*-chlorobenzaldehyde, 5.1 g. (0.055 mole) of sodium propionate and 13.2 g. (0.10 mole) of propionic anhydride was heated at 135° for 18 hours. The warm mixture was poured into 150 ml. of water, stirred thoroughly and neutralized with sodium carbonate. After removal of 2.1 g. (28%) of unchanged *p*-chlorobenzaldehyde by ether extraction, the basic solution was poured, with stirring, into an excess of concentrated hydrochloric acid mixed with cracked ice. Filtration and drying of the solid gave 6.2 g. (60%) of *trans*-3-(*p*-chlorophenyl)-2-methyl-2-propenoic acid (IV), m.p. 167–169°. Admixture of a sample prepared in this manner with that prepared from chlorobenzene and II caused no depression of the melting point.

3,3-Dichloro-2-methyl-2-propenaldoxime.—A mixture of 11 g. (0.08 mole) of 3,3-dichloro-2-methyl-2-propenal, 13.8 g. (0.2 mole) of hydroxylamine hydrochloride and 27.6 g. (0.26 mole) of sodium carbonate in 100 ml. of ethanol was refluxed for 15 hours, filtered while hot, poured into 250 ml. of water and allowed to crystallize. Recrystallization of the product from 50% ethanol yielded 11.0 g. (90%) of 3,3-dichloro-2-methyl-2-propenaldoxime, m.p. 84.5–85.5°. The infrared spectrum in Nujol mull showed the following bands: hydroxyl at 3.07 μ, C–C double bond at 6.29 μ, an intense band at 10.19 μ due to the N–O stretching, and C–Cl stretching frequencies at 10.9, 11.01 and 14.6 μ.

Anal. Calcd. for $C_4H_5Cl_2NO$: C, 31.20; H, 3.25; Cl, 46.05; N, 9.10. Found: C, 31.25; H, 3.00; Cl, 46.66; N, 8.71.

3,3-Bis-ethoxy-1,1-dichloro-2-methyl-1-propene.—3,3-Dichloro-2-methyl-2-propenal (70 g., 0.5 mole) and 100 ml. of absolute ethanol were mixed and allowed to stand for 1.5 hours with a spontaneous temperature rise from 25 to 33°. The solution was then refluxed for 0.5 hour and allowed to cool overnight. Anhydrous hydrogen chloride was bubbled in for 12 hours, with the solution warming to 35° spontaneously. On cooling the product to room temperature, two layers separated and the upper layer was distilled to yield 37.6 g. (35%) of 3,3-bis-ethoxy-1,1-dichloro-2-methyl-1-propene, b.p. 98° (24 mm.), n^{20}_{D} 1.4530–1.4540, d^{30}_{4} 1.042. An undetermined amount of this product codistilled with the starting aldehyde, and attempts to separate this mixture by fractional distillation proved unsuccessful. Infrared analysis indicated about 2% of the starting aldehyde to be present in the analytical sample. The infrared spectrum was compatible with the assigned structure.

Anal. Calcd. for $C_8H_{14}O_2Cl_2$: C, 45.09; H, 6.62. Found: C, 43.98; H, 6.13.

1,1-Bis-(*p*-chlorothiophenyl)-3,3-dichloro-2-methyl-2-propene.—Anhydrous hydrogen chloride was bubbled through a solution of 25.8 g. (0.185 mole) of 3,3-dichloro-2-methyl-2-propenal and 58 g. (0.4 mole) of *p*-chlorobenzenethiol in purified ligroin (b.p. 70°) for three hours. The solution spontaneously warmed from 25° to 40° during the first 0.5 hour. Removal of the solvent from the mixture (and recrystallization from ligroin) yielded 60 g. (75%) of 1,1-bis-(*p*-chlorophenylthio)-3,3-dichloro-2-methyl-2-propene as white platelets, m.p. 65–67°.

Anal. Calcd. for $C_{16}H_{12}Cl_4S_2$: S, 15.63; Cl, 34.57. Found: S, 15.53; Cl, 34.03.

1,1-Bis-(4′,4″-dimethylthiophenyl)-3,3-dichloro-2-methyl-2-propene.—Anhydrous hydrogen chloride was bubbled through a solution of 37 g. (0.267 mole) of 3,3-dichloro-2-methyl-2-propenal and 62 g. (0.5 mole) of *p*-thiocresol in purified ligroin (b.p. 70°) for three hours. During the first 30 minutes, the temperature rose from 20 to 45° and then cooled slowly to room temperature. Cooling to 0° caused precipitation of 70 g. (75%) 1,1-bis-(4′,4″-dimethylthiophenyl)-3,3-dichloro-2-methyl-2-propene. Concentration of the mother liquor and chilling resulted in an additional 5 g. of this product. Recrystallization of the combined product from purified ligroin (b.p. 70°) yielded 70 g. (75%) of product, analytically pure, as white platelets, m.p. 51–52°.

Anal. Calcd. for $C_{18}H_{18}Cl_2S_2$: Cl, 19.20; S, 17.36. Found: Cl, 19.28; S, 17.67.

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MANHATTAN, KAN.