*carboxylate* as pale orange needles, m.p. 108–111°. Sublimation gave an analytical sample, m.p. 110–111°.

*Anal.* Calcd. for $C_{16}H_{12}O_2$: C, 81.33; H, 5.12. Found: C, 81.42; H, 5.11.

*Reaction of diphenylmethane-3,4-diazoöxide with aniline and with benzyl alcohol.* A solution of 0.57 g. of diphenylmethane-3,4-diazoöxide in 10 ml. of pure aniline was plunged into an oil bath preheated to 180°. When gas evolution ceased (3 min.), the reddish black mixture was poured on ice drenched with hydrochloric acid, precipitating a dark red, amorphous solid, 0.50 g., m.p. 205–215° dec. Attempted crystallization by extraction with aqueous alcohol or petroleum ether was not successful, but a benzene solution deposited a presumably purified material (deep red) when diluted with petroleum ether (b.p. 60–70°) and chilled; m.p. 220–221° dec. (bath preheated to 215°). Its identity was not apparent from its analysis, and no more was done with it.

*Anal.* Found: C, 77.92; H, 5.38; N, 8.39.

A similar experiment using benzyl alcohol in place of aniline gave only brown to black, intractable tars.

*Reactions of benzophenone-3,4-diazoöxide with aniline, with benzyl alcohol, and with phenol.* A solution of 0.7 g. of benzophenone-3,4-diazoöxide in 8 ml. of aniline was heated at 180° for 1.5 min., then cooled and poured on ice drenched with excess hydrochloric acid; a dark red solid, 0.73 g., m.p. 200–245°, was obtained. Hot petroleum ether did not dissolve this material significantly, and extraction with hot alcohol yielded only slimes from the extract. Extraction of 0.23 g. with boiling benzene for 3 hr. gave a bright red solution. Washing with dilute sodium hydroxide removed the color, but acidification then gave only 13 mg. of red solid, not further investigated. Evaporation of the benzene solution left a light solid, 0.20 g., m.p. high and indefinite.

*Anal.* Found: C, 74.28; H, 5.08; N, 7.57.

Similar experiments using benzyl alcohol or phenol in place of aniline gave intractable tars accompanied by lesser amounts of amorphous, red solids.

*Reaction of naphthalene-1,2-diazoöxide with silver benzoate triethylamine and methanol.* Following the procedure of Newman and Beal,[7] a solution of 1.0 g. of silver benzoate in 13 ml. of triethylamine was added dropwise to a solution of 0.15 g. of naphthalene-1,2-diazoöxide in 10 ml. of dry methanol. The solution darkened appreciably and a silver mirror formed; no gas evolution was observed. After 0.5 hr., the mixture was filtered and concentrated, but only viscous, black tars could be obtained.

*Reaction of naphthalene-1,2-diazoöxide with benzyl alcohol.* A. *Alone.* A solution of 1.0 g. of naphthalene-1,2-diazoöxide in 10 ml. of benzyl alcohol was plunged into an oil bath preheated to 180°. When gas evolution ceased (3 min.), the mixture was cooled, diluted with 75 ml. of ether, and extracted with three portions of 5% sodium hydroxide, then water, and dried. Acidification of the basic extracts precipitated 0.40 g. (47%) of β-naphthol, m.p. 120–121°, undepressed by mixture with an authentic sample. Treatment of the ethereal solution with 2,4-dinitrophenylhydrazine reagent gave 3.56 g. (212%) of benzaldehyde dinitrophenylhydrazone, m.p. 234–236°, undepressed by mixture with an authentic sample.

B. *In the presence of tri-n-butylamine.* A mixture of 0.5 g. of naphthalene-1,2-diazoöxide, 1 ml. of tri-*n*-butylamine and 6 ml. of benzyl alcohol began to evolve gas at room temperature within a minute of mixing. After 30 min., the mixture was worked up as described in part A, to give 0.19 g. (44%) of β-naphthol, and much benzaldehyde (as dinitrophenylhydrazone).

*Reaction of naphthalene-1,2-diazoöxide with benzylamine* A. *With heat.* A solution of 1.0 g. of naphthalene-1,2-diazooxide in 11 ml. of dry benzylamine was placed in an oil bath preheated to 184°; gas evolution began after a short induction period and lasted for 3 min. The resulting green mixture was poured into dilute hydrochloric acid, precipitating a red oil. It was extracted with three portions of benzene, and the combined extracts were washed with water and dried. Evaporation at the water pump left a red solid, from which was obtained by three recrystallizations from benzene–petroleum ether mixture, 0.45 g. (53%) of β-naphthol, m.p. 120–122°. In another experiment, the drowned reaction mixture was treated with dinitrophenylhydrazine reagent, precipitating a large quantity of the benzaldehyde derivative (identity confirmed by mixed melting point).

*B. At room temperature.* A solution of 0.20 g. of naphthalene-1,2-diazoöxide in 8 ml. of benzylamine was kept at room temperature for 35 min. Work-up as before yielded 0.083 g. (50%) of β-naphthol.

*Effect of benzoyl peroxide on naphthalene-1,2-diazoöxide.* Two solutions were prepared, each consisting of 0.27 g. of naphthalene-1,2-diazoöxide in 7 ml. of benzyl alcohol, and to one was added *ca.* 50 mg. of benzoyl peroxide. Both solutions were then heated at 83° for 4 hr. Workup as before gave no more than traces of β-naphthol from either solution.

ANN ARBOR, MICH.

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

# Reactions of Sodium Methoxide with 2-Alkyl-2,3-dichloroaldehydes. II. Methacrolein Dichloride

SCOTT SEARLES, JR., RAIMOND LIEPINS, AND HARRISON M. KASH

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Reaction of 2,3-dichloro-2-methylpropanal (methacrolein dichloride) with sodium methoxide in methanol gave 1,1-dimethoxy-2,3-epoxy-2-methylpropane (epoxymethacrolein dimethyl acetal, IIc) in 70–80% yield, whereas in dry ether the product is 3-chloro-2-methoxy-2-methylpropanal. In methanol this aldehyde appears to form a relatively stable hemiacetal, thought to be the intermediate in the formation of IIc. The mechanism of the reaction in ether appears to be of the "borderline $S_N2$" type. A third type of reaction, resulting only in substitution of the β-chlorine atom, was observed when the dichloroaldehyde was treated with potassium *t*-butoxide in *t*-butyl alcohol.

It was established recently that α,β-dichloro-α-alkylaldehydes (Ia,b) reacted with two moles of methanolic sodium methoxide to form the corresponding epoxyacetals (IIa,b).[1] These products had previously been assumed to be either 2,3-di-

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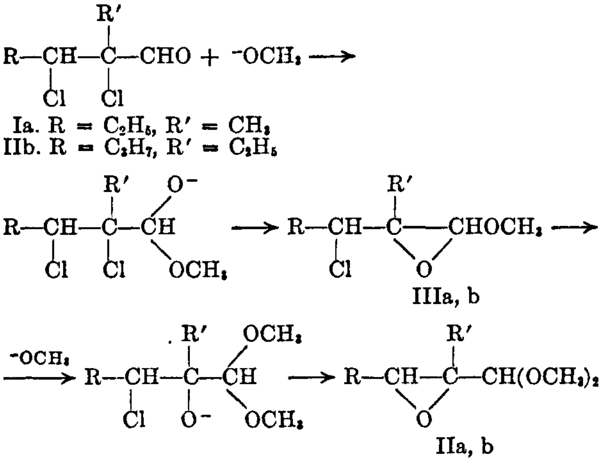
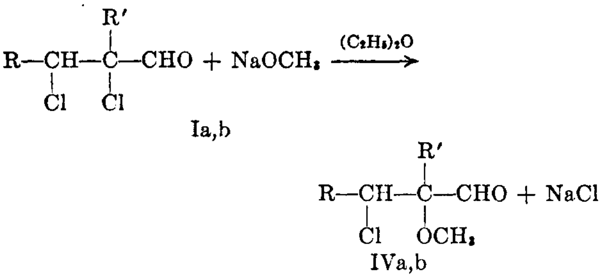
[1] S. Searles, Jr., E. K. Ives, and H. M. Kash, *J. Org. Chem.*, 22, 919 (1957).

methoxyoxetanes or 1,3-dimethoxy-1,2-epoxides.[2-4]

The isolation of a 3-chloro-1-methoxy-1,2-epoxide (IIIb) from the reaction of 2,3-dichloro-2-ethylhexanal with one mole of methanolic methoxide suggested that the reaction proceeded:


Ia. $R = C_2H_5$, $R' = CH_3$
IIb. $R = C_3H_7$, $R' = C_2H_5$

When these reactions were carried out in dry ether, instead of dry methanol, only one chlorine atom was replaced by a methoxyl group even when two to three molecular equivalents of sodium methoxide were used. The products were α-methoxy-β-chloroaldehydes (IVa,b).



These results, both in methanol and ether, were quite different from those of Stevens and coworkers on similar reactions of α-chlorocarbonyl compounds.[5-7] They had reported that in dry ether, α-chlorocarbonyl compounds reacted with sodium methoxide to form epoxyethers, while in dry methanol, α-hydroxyacetals or ketals were formed due to a further reaction with the solvent. We believe that the cause for the different course of reaction with 2,3-dichloroaldehydes is the large steric and electrical effect of the β-chlorine atom.

The simplest member of this 2,3-dichloraldehyde series, 2,3-dichloro-2-methylpropanal (Ic), has now been found to react in the same manner as the previously reported homologs, although at first, due to some experimental artifacts, an entirely different reaction was thought to have taken place. The reaction of this compound with one mole of methanolic sodium methoxide under a variety of conditions gave a product which appeared to be 3-methoxy-2-chloro-2-methylpropanal. This assignment was based on elemental and methoxyl analyses, infrared spectrum, sharp boiling point upon repeated distillations, and chemical tests for chlorine and aldehyde group.

Vapor phase chromatography of this material, however, showed it to be a mixture of two compounds. The retention time of one was identical with that of the starting compound, 2,3-dichloro-2-methylpropanal, while the retention time of the other was identical with that of the dimethoxy compound which was obtained in 70–80% yield by reaction of the dichloride with two molecular equivalents of sodium methoxide. Subsequently, these two pure compounds, boiling points only 5° apart, were isolated by fractional distillation through an efficient spinning band column, and were characterized. There was no evidence of any chloromethoxy compound.

The structure of the dimethoxy compound formed by two molecular equivalents of sodium methoxide was established by an independent synthesis as 1,1-dimethoxy-2,3-epoxy-2-methylpropane. The product of 2-methylacrolein dimethyl acetal and monoperphthalic acid reaction was identical in all physical properties, including vapor phase chromatograph, infrared spectra, and high resolution NMR spectra to that obtained in the two-mole sodium methoxide reaction. NMR spectra gave an elegant confirmation of the structure, showing the two protons of the epoxy ring to be in a different spatial environment and the two methoxyl groups also to be different, apparently because of hindered rotation.

In dry ether, 2,3-dichloro-2-methylpropanal reacted with sodium methoxide to form one product, 3-chloro-2-methoxy-2-methylpropanal (IVc), even in the presence of a large excess of sodium methoxide. The structure of this compound was established by hydrolysis, using dilute sulfuric acid to give a 78% yield of 3-chloro-2-hydroxy-2-methylpropanal (V). The chlorohydrin aldehyde (V), reacted with aqueous sodium carbonate or methanolic sodium methoxide to form impure 2,3-epoxy-2-methylpropanal. The latter was made (Payne[8]) by alkaline hydrogen peroxide epoxidation of 2-methylpropenal. Treatment of the epoxy aldehyde with dilute hydrochloric acid formed both chlorohydrin aldehydes: 3-hydroxy-2-chloro-2-methylpropanal (VI) in 11% yield and 3-chloro-2-hydroxy-2-methylpropanal (V) in 22% yield. Oxidation cleavage of V from the dilute sulfuric acid hydrolysis of the

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(2) J. Lichtenberger and M. Naftali, *Bull. soc. chim.*, 4 (5), 325 (1937).

(3) A. Kirrmann and J. Lichtenberger, *Compt. rend.*, 205 1259 (1939).

(4) F. Krausz, *Ann. chim.*, 4 (12), 811 (1949).

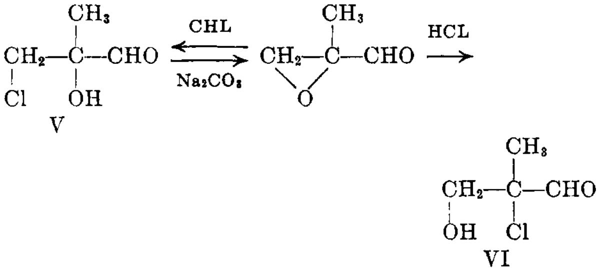
(5) C. L. Stevens and E. Farkas, *J. Am. Chem. Soc.*, **74,** 618 (1952).

(6) C. L. Stevens, E. Farkas, and B. Gillis, *J. Am. Chem. Soc.*, **76,** 2695 (1954).

(7) C. L. Stevens and B. T. Gillis, *J. Am. Chem. Soc.*, **79,** 3448 (1957).

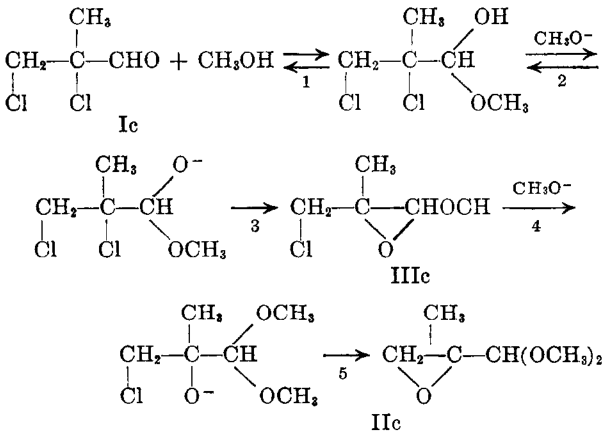
(8) G. B. Payne, *J. Am. Chem. Soc.*, **81,** 4901 (1959).

ethereal sodium methoxide reaction product with periodic acid gave chloroacetone in practically quantitative yield. The structure of VI was established by the fact it is an isomer of V with the same functional groups.



These strikingly diverse results may be due, at least in part, to reaction of the aldehyde with methanol. 2,3-Dichloro-2-methylpropanal and methanol interact rapidly without catalyst to form a relatively stable hemiacetal. This was shown by the large amount of heat evolved on mixing, the practically total loss of the carbonyl bands, the appearance of characteristic hemiacetal bands[9,10] in the infrared spectrum, and the large positive deviation in the index of refraction of the mixture,[11-13] the maximum occurring in an approximately equimolar mixture. The hemiacetal can be distilled from the mixture under reduced pressure, but on standing it dissociates to some extent. A value of 23 was determined spectrally for the equilibrium constant for formation of the hemiacetal in methanol solution at 30°.

It seems likely, therefore, that the reaction observed with methanolic sodium methoxide is actually with the hemiacetal of the dichloroaldehyde, rather than with the aldehyde directly. In this mechanism[14] step 3, forming IIIc, must be slower than the subsequent steps, since none of IIIc could be detected in reaction with one mole of sodium methoxide in spite of the use of a variety of experimental conditions.[15] Furthermore, methanolysis of IIIc can not be occurring because the yield of IIc was less than 50% (in fact, never more than 32%) when one mole of sodium methoxide was used. If methanolysis were occurring, either the yield of IIc should have been as high with one mole of sodium methoxide as with two, or 3-chloro-2-hydroxy-2-methylpropanal dimethyl acetal should have been formed. No appreciable quantities of any materials were evident except the epoxyacetal and the starting compound.



In ether the reaction of the dichloroaldehyde itself must be observed. The lack of reaction at the carbonyl group is due, as pointed out earlier,[1] to the shielding of the latter by the β-chlorine atom, in conjunction with the α-chlorine and α-methyl group. Adjacent carbonyl groups strongly activate halogen atoms with regard to ease of substitution, apparently overcoming in this case the unfavorable tertiary nature of the α-chlorine atom. Involved here may be the so-called "borderline $S_N2$"[16] mechanism, in which the bond breaking is more important than bond making. The transition state in this mechanism is more polar than in the ordinary $S_N2$ mechanism, due to delocalization of electrons involving the carbonyl group and longer partial bonds,[16] as skillfully stated recently by Zimmerman and Ahramjian.[17] This results in the reaction's being less subject to steric hindrance at the α-carbon than is usual for $S_N2$ reactions.

A third possible course of reaction, substitution of the β-chlorine atom by the alkoxy group, was apparently observed in the reaction of 2,3-dichloro-2-methylpropanal with potassium *t*-butoxide in *t*-butanol. The product isolated by distillation was 3-hydroxy-2-chloro-2-methylpropanal, which could reasonably have formed from thermal pyrolysis of initially formed 3-*t*-butoxy-2-chloro-2-methylpropanal during distillation with loss of isobutylene.

The failure of this alkoxide to react at either the carbonyl group or the α-carbon atom is probably because of its bulk and the shielding about these positions. No hemiacetal formation was observed with *t*-butanol and the dichloroaldehyde. Thus, the reaction was restricted here to the relatively slow substitution process at the β-position.

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(9) G. B. B. M. Sutherland, *Trans. Faraday Soc.*, **41**, 206 (1945).

(10) A. Ashdown and T. A. Kletz, *J. Chem. Soc.*, 1454 (1948).

(11) I. Lauder, *Trans. Faraday Soc.*, **44**, 734 (1948).

(12) G. W. Meadows and B. deB. Darwent, *Trans. Faraday Soc.*, **48**, 1015 (1952).

(13) F. E. McKenna, H. V. Tartar, and E. C. Lingafetter, *J. Am. Chem. Soc.*, **75**, 604 (1953).

(14) A similar mechanism would apply to the homologous cases previously reported (ref. 1).

(15) Step 3 might not be the slowest one in the sequence for the reaction of homologous compounds; with 2,3-dichloro-2-ethylhexanal (Ib), the isolation of IIIb indicates that step 4 is slower. This is probably due to the bulk of the adjacent ethyl and propyl groups in that case.

(16) R. E. Parker and N. S. Isaacs, *Chem. Revs.*, **59**, 737 (1959).

(17) H. E. Zimmerman and L. Ahramjian, Am. Chem. Soc. Meeting Abstracts, Sept. 13–18, 1959, p. 1P.

## EXPERIMENTAL

*2,3-Dichloro-2-methylpropanal.* Dry chlorine was bubbled slowly with stirring into 250 g. of α-methylacrolein, kept at −5° to −10° and protected from light. When absorption of chlorine ceased, the material was distilled through a 6-inch glass helices-packed column to give 30 g. (12%) of recovered α-methylacrolein and 360 g. (71%) of a liquid, b.p. 72–73° (60 mm.), $n_D^{20}$ 1.4558 (reported b.p. 147°[18]). An elemental analysis was carried out, since none was reported previously.[18]

*Anal.* Calcd. for $C_4H_6OCl_2$: C, 34.1; H, 4.29. Found: C, 33.9; H, 4.33.

It formed a 2,4-dinitrophenylhydrazone, m.p. 122–122.5°.

Chlorination of α-methylacrolein in chloroform solution was generally less satisfactory than without solvent because of the tendency for chlorination to proceed beyond the dichloride stage giving 2,3-dichloro-2-methylpropionyl chloride, b.p. 80–82° (60 mm.), $n_D^{20}$ 1.4690. Treatment of the latter with methanol and distillation gave the methyl ester, b.p. 170–172°, $n_D^{20}$ 1.4510, identical in infrared spectrum and other properties with methyl 2,3-dichloro-2-methylpropionate, b.p. 170–172°, $n_D^{20}$ 1.4504, obtained by chlorination of authentic methyl α-methylacrylate; reported[19] for this ester b.p. 170–171° and $n_D^{20}$ 1.4545.

*Reaction of 2,3-dichloro-2-methylpropanal with one mole of methanolic sodium methoxidel.* 2,3-Dichloro-2-methylpropanal (254 g.) was added at a fast drop rate to a stirred solution of 39.1 g. of sodium in 1.5 l. of methanol cooled in an ice bath. The solution was warmed to room temperature and was stirred for 15 hr. The precipitated sodium chloride was removed by filtration, washed with cold methanol. Distillation gave 150 g. of a material, b.p. 61–65° (30 mm.), $n_D^{20}$ 1.4334. This is a 65% yield of the 1:1 mixture of 2,3-dichloro-2-methylpropanal and 1,1-dimethoxy-2,3-epoxy 2-methylpropane.

*Anal.* Calcd. for $C_5H_9O_2Cl$: C, 43.9; H, 6.64. Found: C, 43.6; H, 6.47.

Vapor phase chromatography of this material through a 4-foot column at 100° and a flow rate of 97 ml. per min. on tricresyl phosphate produced two components, one with a retention time of 44.4 min., the other with 53.8 min. These retention times were identical with those of pure 1,1-dimethoxy-2,3-epoxy-2-methylpropane and pure 2,3-dichloro-2-methylpropanal, respectively.

Fractionation of the material through a Piros-Glover spinning band distillation column gave the first fraction as essentially pure 2,3-dichloro-2-methylpropanal, b.p. 75° (70 mm.), $n_D^{20}$ 1.4510 and last fraction as essentially pure 1,1-dimethoxy-2,3-epoxy-2-methyl-propane, b.p. 80° (70 mm.), $n_D^{20}$ 1.4257. The intermediate fractions appeared to be mixtures of the two components.

*1,1-Dimethoxy-2,3-epoxy-2-methylpropane.* To a stirred, ice-cooled solution of sodium methoxide, prepared by dissolving 13.3 g. of sodium in 500 ml. of dry methanol, was added 49 g. of 2,3-dichloro-2-methylpropanal at a slow drop rate. The solution was allowed to warm up to room temperature and was stirred for 22 hr. The precipitated sodium chloride was removed by filtration, washed with cold methanol. Distillation gave 28.5 g. (75%) of 1,1-dimethoxy-2,3-epoxy-2-methylpropane, b.p. 53–55° (20 mm.), $n_D^{20}$ 1.4158.

*Anal.* Calcd. for $C_6H_{12}O_2$: C, 54.5; H, 9.15; $OCH_3$, 47.0. Found: C, 54.5; H, 8.73; $OCH_3$, 46.8.

*Reaction of potassium t-butoxide with 2,3-dichloro-2-methylpropanal.* A solution of potassium *t*-butoxide in butanal (6.9 g. of potassium in 500 ml. *t*-butanol) was added dropwise with stirring to a cooled solution of 2,3-dichloro-2-methylpropanal (25 g.) in 200 ml. of *t*-butanol. The solution was stirred at room temperature for 16 hr. Distillation left a semisolid residue which was extracted with chloroform and distillation of the extracts gave 4 g. (19%) of a material, b.p. 57–63° (15 mm.), $n_D^{20}$ 1.4540. Its infrared spectrum contained absorption bands at 2.90, 5.70, 9.35, and 13.2–13.5 μ, characteristic of a primary hydroxyl, saturated aldehyde, and a carbon-chlorine bond. This material appears to be 3-hydroxy-2-chloro-2-methylpropanal, since its infrared spectrum, boiling point, and index of refraction were practically identical with those properties of the 3-hydroxy-2-chloro-2-methylpropanal obtained from the reaction of hydrochloric acid with 2,3-epoxy-2-methylpropanal, described below.

*1,1-Dimethoxy-2,3-epoxy-2-methylpropane by epoxidation.* α-Methylacrolein dimethyl acetal, b.p. 103–105°, $n_D^{20}$ 1.4041 (lit.[20] b.p. 102°) was obtained in a 78% from α-methylacrolein and methyl orthoformate. Its infrared spectrum was in accord with the assigned structure, showing no carbonyl absorption but absorption bands for the terminal double bond (3.6, 6.0, and 11.3 μ). A solution of 20 g. of α-methylacrolein dimethyl acetal and approximately 0.22 mole of monoperphthalic acid[21] (as determined by titration[21] and used directly) in 450 ml. of ether was kept at 0° for 60 hr. Extraction of the etherate with 10% potassium carbonate and distillation gave 10 g. (50%) of unchanged α-methylacrolein dimethyl acetal, b.p. 100–108°, $n_D^{20}$ 1.4087 and 2 g. (18%)[22] of 1,1-dimethoxy-2,3-epoxy-2-methylpropane, b.p. 55–57° (20 mm.), $n_D^{20}$ 1.4140. The infrared spectrum of this material had bands at 7.50, 7.70, 11.90, and 13.0 μ, which were not present in the spectrum of the unsaturated acetal, and it was identical in all respects with that of the product from the reaction of sodium methoxide with 2,3-dichloro-2-methylpropanal.

*3-Chloro-2-methoxy-2-methylpropanal.* To 56 g. of anhydrous sodium methoxide in 600 ml. of anhydrous ice-cooled ether was added dropwise with stirring 66 g. of 2,3-dichloro-2-methylpropanal in 200 ml. of anhydrous ether. After being stirred at room temperature for 24 hr., the now-bright orange solution was filtered and fractionally distilled to yield 38 g. (60%) of 3-chloro-2-methoxy-2-methylpropanal, b.p. 63–64° (18 mm.), $n_D^{20}$ 1.4323. The infrared spectrum showed a strong absorption band at 5.7 μ but no absorptions characteristic of an epoxide.

*Hydrolysis of 3-chloro-2-methoxy-2-methylpropanal.* 3-Chloro-2-methoxy-2-methylpropanal (20 g.) was added slowly to 100 ml. of ice-cooled 1*N* sulfuric acid solution. After being warmed on a steam bath for 3 hr. and left at room temperature for 20 hr., the light yellow solution was neutralized with a saturated solution of sodium bicarbonate, saturated with ammonium sulfate, extracted with chloroform, followed by a 55-hr. continuous ether extraction. The combined extracts were dried over magnesium sulfate and fractionally distilled giving 14 g. (78%) of 3-chloro-2-hydroxy-2-methylpropanal, b.p. 60–65° (0.8 mm.), $n_D^{20}$ 1.4650 (immediately after distillation; a few days later it changed to $n_D^{20}$ 1.4885 with a considerable increase in viscosity; this change may be due to dimerization, common with α-hydroxyaldehydes[23–27]).

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(18) H. Schulz and H. Wagner, *Angew. Chem.*, **62**, 105 (1950).

(19) P. Bieber, *Bull. soc. chim. France*, 199 (1954).

(20) S. Zeisel and M. Daniek, *Monatsh.*, **30**, 727 (1909).

(21) E. C. Horning, *Org. Syntheses*, **Coll. Vol. III**, 619 (1955).

(22) Subsequent work in these laboratories on other unsaturated acetals has shown that much higher yields can be obtained if the epoxidation is carried out at room temperature.

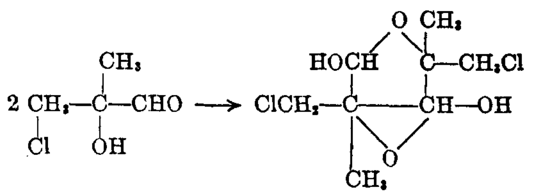
(23) R. Dworzak, and P. Pfifferling, *Monatsh*, **48**, 251 (1927).

(24) A. Kirrmann and P. Chancel, *Bull. soc. chim. France*, 711 (1950).

(25) W. E. Parham, H. Wynberg, and F. L. Ramp, *J Am. Chem. Soc.*, **75**, 2065 (1953).

(26) W. E. Parham and H. E. Reiff, *J. Am. Chem. Soc.*, **77**, 6391 (1955).

(27) C. L. Stevens and B. T. Gillis, *J. Am. Chem. Soc.*, **79**, 3448 (1957).



*Anal.* Calcd. for $C_4H_7O_2Cl$: C, 39.2; H, 5.76. Found: C, 39.6; H, 5.62.

An interesting polymorphism was observed with the *p*-nitro- and 2,3-dinitrophenylhydrazones of this compound. The 2,4-dinitrophenylhydrazone existed in two forms: m.p. 114° and 165°, while the *p*-nitrophenylhydrazone had three forms: m.p. 106°, 115°, and 129°. If the lowest melting modification is slowly heated, the other modifications may be observed in succession.

*Anal.* Calcd. for $C_{10}H_{11}O_5N_4Cl$: C, 39.7; H, 3.66. Found: C, 39.9; H, 3.36.

*Chloroacetone.* A solution of 3.2 g. of 3-chloro-2-hydroxy-2-methylpropanal in 20 ml. of hot water was cooled and added to a solution of 5.95 g. of periodic acid in 303 ml. of water, neutralized to *p*H 7.0 with sodium bicarbonate. As soon as the solutions were mixed, lacrimatory vapors were given off. After the solution was kept at room temperature for 24 hr., it was neutralized, extracted with chloroform, and the magnesium sulfate–dried extracts were fractionally distilled, giving 2.3 g. (95%) of chloroacetone, b.p. 117–119°, (lit.[28] b.p. 119°), 2,4-dinitrophenylhydrazone, m.p. 123.5–124° (lit.[29] m.p. 125°). A mixed melting point with 2,4-dinitrophenylhydrazone of acetone (both have the same melting point) gave a depression.

*Alkaline hydrogen peroxide epoxidation of 2-methylpropenal.* A mixture of 75.1 g. of 2-methylpropenal and 12.3 g. of 30% hydrogen peroxide was agitated and added dropwise to stirred and cooled (25–35°) aqueous sodium hydroxide, the *p*H of which was maintained at 8.0–8.5 by constant addition of 1*N* sodium hydroxide. The solution was stirred at room temperature for an additional hour, then saturated with ammonium sulfate, extracted with chloroform, and extracts were dried over magnesium sulfate and fractionally distilled to give 25 g. (27%) of anhydrous 2,3-epoxy-2-methylpropanal, b.p. 53–54° (80 mm.), $n_D^{20}$ 1.4220 [reported[8] b.p. 52–53° (80 mm.)].

*Dilute hydrochloric acid hydrolysis of 2,3-epoxy-2-methylpropanal.* After adding 14.8 g. of 2,3-epoxy-2-methylpropanal to 200 ml. of 1*N* hydrochloric acid, the solution was warmed for about 3 hr. The cooled solution was neutralized with sodium bicarbonate, saturated with ammonium sulfate, and extracted with chloroform. The magnesium sulfate–dried extracts were fractionally distilled giving 2 g. (11%) of a material, b.p. 80–85° (23 mm.), $n_D^{20}$ 1.4560 and 4 g. (22%) of 3-chloro-2-hydroxy-2-methylpropanal, b.p. 140–145° (23 mm.), $n_D^{20}$ 1.4860, in addition to about 3 g. of a high boiling residue. The infrared spectrum of the material from the first fraction contained absorption bands at 2.90, 5.72 (strong), 7.50, 9.20, and 13.3–13.4 μ, which was very similar to that of the second fraction, bands at 2.90, 5.75 (medium), 7.25, 9.0–9.3, 9.1–10.0, and 13.3–13.4 μ, which are characteristic of a hydroxyl, a saturated carbonyl, and a carbon-chlorine bond.

The 2,4-dinitrophenylhydrazone of the material from the second fraction gave no depression with that from the ethereal sodium methoxide reaction. After several weeks of standing, this material had formed some white solid which may be the dimer mentioned earlier.

The material from the first fraction was an isomer of that from the second fraction.

*Anal.* Calcd. for $C_4H_7O_2Cl$: C, 39.2; H, 5.76. Found: C, 38.6; H, 5.5.

The 2,4-dinitrophenylhydrazone of the material from the first fraction had a melting point 120–121° and gave a 7–10° depression on mixture with the 2,4-dinitrophenylhydrazone of 3-chloro-2-hydroxy-2-methylpropanal obtained from the ethereal sodium methoxide reaction.

*Anal.* Calcd. for $C_{10}H_{11}O_5N_4O$: C, 39.7; H, 3.66; N, 18.51. Found: C, 39.8; H, 3.72; N, 18.50.

*Reaction of 2,3-dichloro-2-methylpropanal with methanol.* 2,3-Dichloro-2-methylpropanal (10 g.) was added to 25 g. of cooled, dry methanol. Heat was liberated as the addition was carried out. The solution was agitated at room temperature for about 2 hr. Fractional distillation gave 2.2 g. (18%) of a material, b.p. 35–38° (19 mm.). Its infrared spectrum was in accord with the assigned structure, showing no carbonyl absorption but characteristic absorption bands (9.05, 9.80, and 11.85 μ) for a hemiacetal.[9,10] Redistillation produced a material, the infrared spectrum of which contained a carbonyl absorption for a saturated aldehyde.

The refractive index of 2,3-dichloro-2-methylpropanol-methanol solutions showed maximum deviation at 45–50 mole % methanol (as shown in Table I), indicating 1:1 compound formation.

TABLE I

REFRACTIVE INDICES OF 2,3-DICHLORO-2-METHYLPROPANAL-METHANOL SOLUTIONS

| Mole % $CH_3OH$ | $n_D^{20}$ |
|---|---|
| 0.20 | 1.4668 |
| 0.45 | 1.4698 |
| 0.49 | 1.4697 |
| 0.55 | 1.4690 |
| 0.70 | 1.4664 |
| 0.95 | 1.4610 |

An estimation of the extent of hemiacetal formation was carried out by means of infrared spectra by measuring the area of the 5.70 μ carbonyl band and comparing with the areas in the infrared spectra of solutions of known concentration. The spectra were obtained with the double beam Perkin-Elmer Infracord, using matched cells. A solution of 50 mole % of 2,3-dichloro-2-methylpropanal in methanol had the same carbonyl absorption as a 4% solution of 2,3-dichloro-2-methylpropanal in ether, the determinations being made at 30°. This corresponds to only 4% of the free aldehyde in the former case indicating a 96% conversion to the hemiacetal. The equilibrium constant for the formation of hemiacetal, K = [hemiacetal]/[aldehyde][methanol], is 23.

Corresponding estimation of the hemiacetal formation in *t*-butyl alcohol gave 5% as the average value for the amount of aldehyde converted to hemiacetal. This might have been due to solvent effects rather than an actual hemiacetal formation.

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