[CONTRIBUTION NO. 241 FROM THE CHEMICAL DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS & COMPANY]

# Interchange Reactions of Orthothioformates and Mercaptoles

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Interchange reactions of carboxylic esters and alcohols have been known for some years,[3] and the related interchanges in the cases of ortho esters[4] and of ketals[5] have been reported. Work in this Laboratory has now shown that oxygen-for-sulfur interchanges in orthiothioformates and mercaptoles[6] can be readily carried out, furnishing a convenient means of preparation of orthoformates and ketals.[7] Thus, in the presence of a catalyst such as zinc chloride the following reactions take place.

$$HC(SC_2H_5)_3 + 3ROH \longrightarrow HC(OR)_3 + 3C_2H_5SH \quad (1)$$

$$(CH_3)_2C(SC_2H_5)_2 + 2ROH \longrightarrow (CH_3)_2C(OR)_2 + 2C_2H_5SH \quad (2)$$

Since the orthothioformates and mercaptoles are easily prepared in nearly quantitative yields, the corresponding orthoformates and ketals frequently can be prepared more easily by the above reactions than by more conventional means. These interchanges were found to be equilibrium reactions and can be shifted to give high yields of the desired ortho esters or ketals by removal of the low-boiling thiol. Evidence for the reverse of reaction (1) above exists in the reported preparation of an orthothioformate from ethanedithiol and ethyl orthoformate,[8] with the liberation of ethanol, but the equilibrium nature of the reaction was not demonstrated. These reactions are normally very slow, but they may be greatly accelerated by Friedel–Crafts type catalysts. While strong acids, such as sulfuric or *p*-toluenesulfonic, at elevated temperatures were found to decompose the oxygen ortho esters in some cases,[9] forming normal esters and the corresponding ethers, such catalysts were satisfactory for the preparation of ketals. However, the ketals should not be worked up in the presence of acid since they may be converted to unsaturated ethers.[10]

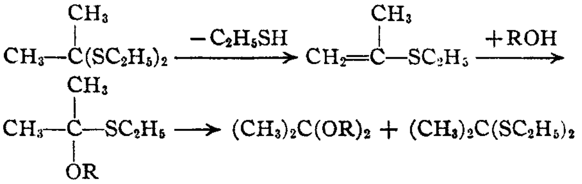
The mechanism of these reactions has not been established. However, from the type of catalyst involved it would appear that the mechanism is ionic in nature and may be identical with that for the acid-catalyzed formation of ketals from ketones and orthoformates. Post has proposed a mechanism for the latter reaction[11] and, by analogy, the following stepwise addition mechanism may be postulated for the reaction of an alcohol with ethyl orthothioformate.

$$HC(SC_2H_5)_3 + H^+ \rightleftharpoons HC(SC_2H_5)_2S(H^+)C_2H_5 \rightleftharpoons$$

$$C_2H_5SH + HC^+(SC_2H_5)_2 \overset{ROH}{\rightleftharpoons} HC(SC_2H_5)_2OR + H^+$$

$$HC(SC_2H_5)_2OR \rightleftharpoons HC(SC_2H_5)(OR)_2 \rightleftharpoons HC(OR)_3$$

In support of the proposed stepwise addition mechanism in the mercaptole interchange is the the isolation of a high-boiling, sulfur-containing compound believed to be the monothioketal. In the mercaptole reaction, however, there is the possibility of formation of an unsaturated sulfide by the elimination of one mole of thiol,[12] followed by the addition of alcohol to give a monothioketal[13] which could disproportionate to yield the ketal and mercaptole.[14] However, no sulfur compounds boiling in the range of the expected unsaturated sulfides were found in the reaction mixtures.



$$CH_3\text{—}\overset{CH_3}{\overset{|}{C}}(SC_2H_5)_2 \xrightarrow{-C_2H_5SH} CH_2\text{=}\overset{CH_3}{\overset{|}{C}}\text{—}SC_2H_5 \xrightarrow{+ROH}$$

$$CH_3\text{—}\underset{OR}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}\text{—}SC_2H_5 \longrightarrow (CH_3)_2C(OR)_2 + (CH_3)_2C(SC_2H_5)_2$$

## Experimental

**Ethyl Orthoformate.**—A mixture of 98 g. (0.5 mole) of ethyl orthothioformate[15] and 92 g. (2.0 moles) of absolute ethanol was refluxed with 2 g. of fused zinc chloride for ten hours while 90% of the theoretical amount of ethanethiol was slowly removed by distillation at 35–37° through a 20-inch Fenske ring-packed column with adjustable take-off head. The remaining material was distilled and, after removal of the excess ethanol, 49 g. (66% yield) of ethyl orthoformate was collected at 144–146°, $n^{24}D$ 1.3917.

**Butyl Orthoformate.**—A mixture of 39.2 g. (0.2 mole) of ethyl orthothioformate and 59 g. (0.8 mole) of *n*-butanol was refluxed with 1 g. of fused zinc chloride for six hours during which time 91% of the theoretical thiol was liberated and removed by distillation. The reaction mixture was cooled and washed with water to remove the catalyst. The product was dried with anhydrous sodium sulfate and distilled to yield 12 g. (46%) of butyl orthoformate distilling at 240–244°, $n^{23}D$ 1.4198.

From a mixture of 58.8 g. (0.3 mole) of ethyl orthothioformate and 89 g. (1.2 moles) of *n*-butanol refluxed

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(3) Fehlandt and Adkins, THIS JOURNAL, **57**, 193 (1935); Hatch and Adkins, *ibid.*, **59**, 1694 (1937).

(4) (a) Hunter, *J. Chem. Soc.*, **125**, 1389 (1924); (b) Post and Erickson, THIS JOURNAL, **55**, 3851 (1933); (c) Helferich and Reimann, *Ber.*, **80**, 163 (1947).

(5) Post, THIS JOURNAL, **55**, 4176 (1933).

(6) Hanford and Mochel, U. S. Patent 2,229,651 (1941); Mochel, U. S. Patent 2,229,665 (1941).

(7) Interchange reactions of thiol esters with alcohols and, less readily, with thiols, were also demonstrated during the course of this research.

(8) Hurtley and Smiles, *J. Chem. Soc.*, 2263 (1926).

(9) *Cf.* Staudinger and Rathsam, *Helv. Chim. Acta*, **5**, 645 (1922).

(10) Killian, Hennion and Nieuwland, THIS JOURNAL, **57**, 544 (1935).

(11) Post, *J. Org. Chem.*, **5**, 244 (1940).

(12) Sporzynski, *Arch. Chem. Farm.*, **3**, 59 (1936).

(13) Norris, Verbanc and Hennion, THIS JOURNAL, **60**, 1159 (1938).

(14) Wenzel and Reid, *ibid.*, **59**, 1090 (1937).

(15) Prepared in nearly quantitative yield from ethyl formate and ethanethiol by the method of Holmberg, *Ber.*, **40**, 1740 (1907).

with 1 ml. of concentrated sulfuric acid for thirty minutes and then distilled there was obtained nearly the theoretical yield of ethanethiol at 35–40°. Fractionation of the residue directly gave 30 g. (98% yield) of *n*-butyl formate, b. p. 107–110°, $n^{25}$D 1.4896, and 36 g. (93%) of *n*-butyl ether, b. p. 140–141°, $n^{25}$D 1.4005.

**2,2-Dimethoxybutane.**—A mixture of 178 g. (1 mole) of 2,2-di-(ethylmercapto)-butane,[16] 128 g. (4 moles) of methanol and 3 g. of hydrogen chloride was heated under a 20-inch Fenske ring-packed column with adjustable take-off head, and ethanethiol was removed as formed. After fourteen hours, 119 g. of distillate had been removed at 35–40°. By iodine titration this was shown to contain 85% of ethanethiol, indicating that 82% of the theoretical ethanethiol had been removed. The residue was made very slightly alkaline with sodium methoxide and distilled. At 40–65° there was collected 98 g. of methanol and methanol/ketal binary. The column was then put under 100 mm. pressure and a fraction taken off at 50–51° (100 mm.). This consisted of 58 g. (49% yield) of 2,2-dimethoxybutane,[17] $n^{21}$D 1.3878. An additional 5 g. was obtained by pouring the methanol fraction into a large volume of water, separating and distilling the organic layer. Assuming a stepwise exchange with a complete first step, the yield of ketal isolated was 83% of theoretical as indicated by thiol obtained. A high boiling fraction, 93–102° (100 m.), was obtained by further distillation. This contained sulfur and liberated more thiol on treatment with methanol and acid; it presumably was the 2-methoxy-2-(ethylmercapto)-butane but it was not purified and analyzed.

In another experiment using *p*-toluenesulfonic acid as catalyst and a 500% excess of methanol, a 91% yield of a 2,2-dimethoxybutane/methanol constant boiling mixture containing 25% of the ketal was obtained at 65°. The pure ketal was isolated by drowning the mixture in water, separating and distilling the organic layer.

Following the standard procedure for the preparation of mercaptoles, 2,2-di-(cyclohexylmercapto)-butane was prepared in 57% yield; b. p. 175–176° (3 mm.), $n^{23}$D 1.5305.

*Anal.* Calcd. for $C_{16}H_{30}S_2$: S, 22.37. Found: S, 21.92.

In a 1-liter flask was placed 160 g. (0.55 mole) of 2,2-di-(cyclohexylmercapto)-butane, 110 ml. of methanol (500% excess) and 8.1 g. of dry *p*-toluenesulfonic acid. This mixture was heated under a small column and distillate slowly collected at 64°. After two and one-half hours an additional 700 ml. of methanol was added. At the end of five and one-half hours the temperature had reached 70° and the distillate amounted to 210 g. Redistillation of this distillate yielded 204 g. of a 2,2-dimethoxybutane/methanol mixture boiling at 65°, $n^{23}$D 1.3330. This binary contained 10% of the ketal, or 31% of the theoretical yield.

## Summary

It has been found that alcohols react with orthothioformates or mercaptoles in the presence of acidic catalysts to yield the corresponding orthoformates or ketals, or their decomposition products.

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RECEIVED FEBRUARY 26, 1948

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[16] Mann and Purdie, *J. Chem. Soc.*, 1549 (1935).

[17] Killian, Hennion and Nieuwland, THIS JOURNAL, **56**, 1384 (1934).

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

# The Exchange Reaction between Methane and Deuteromethanes on Silica–Alumina Cracking Catalysts

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The following research originated in a discussion at the Gibson Island Conference on Catalysis, June 1941, in which one of us (H. S. T.) suggested that the cracking of petroleum hydrocarbons on silica–alumina catalysts should be initiated by the breaking of, at least, one C–H bond in the hydrocarbon molecule. Otherwise, it was not possible for the carbon core of a hydrocarbon chain to come within the radius of chemical interaction with the catalyst surface. The plausibility of such a view is at once evident by inspection of a molecular model of a hydrocarbon molecule, as constructed with the Fisher–Hirschfelder atom models. At the same time, the suggestion was viewed by some with skepticisim, since it was believed that the idea could not be put to experimental test.

A study of the exchange reaction between hydrocarbons and deuterohydrocarbons in contact with silica–alumina catalysts permits, however, a direct and convincing test of the idea, and under quite stringent conditions.

It is generally agreed, from the known stability of the methane molecule, that if exchange can be demonstrated between methane and deuteromethanes at temperatures below those at which catalytic cracking of higher hydrocarbons is carried out, there can be no reasonable doubt that, in the cracking reaction, the C–H bonds must be readily and freely broken as postulated. The preliminary exploration of this reaction was carried out by Mr. E. F. Hammel in 1941. The quantitative examination of the process is recorded in the following paragraphs.

## Experimental Details

**Materials.**—Methane from a commercial tank was used, without purification. A mass spectrographic analysis showed a purity of ~96%. Deuteromethanes were prepared by means of the reaction between heavy water and aluminum carbide. The deuterium oxide employed came from our supply of heavy water. The deuterium oxide distilled over C. P. aluminum carbide, and the temperature was raised to 70°. At this temperature the reaction proceeds very smoothly. It was found that, at room temperature, no reaction takes place, in agreement with Urey and Price.[2] The gas collected showed with the mass spectrometer the following composition: $CD_4$ 40%, $CD_3H$ 5.7%, $CH_2D$ 1%, $CH_3D$ 0.3%, $CH_4$ 53%.[3]

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[2] H. C. Urey and D. Price, *J. Chem. Phys.*, **2**, 800 (1934).

[3] This gas composition is abnormal. It can only have been produced by successive interactions of $H_2O$ and of $D_2O$ with the carbide. Since the heavy water used was of high purity we can only conclude that the carbide sample used held tenaciously by adsorption the light water and that this reacted first before the heavy water came in contact with the catalyst.