the production of 10 to 15% of unsaturated compounds with *iso*propyl alcohol. This latter fact indicates that the oxide catalysts were not completely reduced to the metals. The production of saturated hydrocarbons is rather small in all other cases. Acid production was found to be small and fairly constant for the same alcohols over different catalysts.

The plated catalysts were found to be unsatisfactory because the high temperature of reaction apparently caused solution of the plated metal into the supporting metal. It also seems likely that the reaction takes place throughout the catalyst. Evidence for this view is found in the change in mechanical properties of the gauzes, wire and pellets, and in the reduction of copper oxide to metallic copper in the center of pellets of a copper oxide–vanadium oxide mixture.

The temperature of the reaction varied with the alcohol–air ratios and with the catalysts employed. The copper–vanadium, copper–molybdenum and copper–tungsten oxide mixtures were comparatively inactive and external heating was necessary. Heat was also applied to maintain a reaction at the surface of the 50% zinc–copper alloy.

The fact that small amounts of material incorporated into the metallic catalysts produce no marked effect indicates that a larger portion of the surface of the catalyst is active in the catalytic oxidation of alcohols.

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[CONTRIBUTION FROM THE PEARSON MEMORIAL LABORATORY OF TUFTS COLLEGE]

THE ADDITION OF SODIUM MALONIC ESTER TO ALIPHATIC MUSTARD OILS

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Phenylisothiocyanate reacts smoothly with substances containing an active methylene group, such as malonic ester, acetoacetic ester and acetylacetone, forming sulfur derivatives that have been shown[1] to be useful for the preparation of heterocyclics of the isoxazole and pyrazole series. Similar transformations might be expected starting with methylisothiocyanate; accordingly, with the hope of extending the scope of these reactions so as to include the aliphatic mustard oils, work has been resumed on the chemistry of the isothiocyanates. It first became necessary to synthesize the desired thio-amides, for methyl mustard oil, which is far more expensive and more difficult to prepare than phenyl mustard oil, has been much less studied. No such work has been done with it. This communication deals with the action of several alkyl mustard oils on dimethyl and diethyl malonate.

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[1] Worrall, THIS JOURNAL, **42**, 1055 (1920); **44**, 1551 (1922); **45**, 3092 (1923); **46**, 2832 (1924).

Sodium diethyl malonate and methyl mustard oil react as follows.

$$NaCH(COOC_2H_5)_2 + CH_3NCS = CH(COOC_2H_5)_2C(SNa)NCH_3$$

The product is soluble in cold water, from which it is precipitated by the addition of hydrochloric acid.

$$CH(COOC_2H_5)_2C(SNa)NCH_3 + HCl = NaCl + CH(COOC_2H_5)_2C(SH)NCH_3$$
$$CH(COOC_2H_5)_2C(SH)NCH_3 = CH(COOC_2H_5)_2CSNHCH_3$$

The last equation is reversible, for the thio-amide is soluble in aqueous alkali. Therefore, carbethoxy ethylmalonate monothiomethylamide is a typical tautomeric substance existing in the form of an equilibrium mixture.

Similar products were obtained with ethyl, propyl, butyl, amyl and benzyl mustard oils. The yields were excellent in all cases, approximately 80% of the theoretical as a rule. In one instance the crude product accounted for 87% of the material used. These thio-amides are oils or low-melting solids, insoluble of course in water but very easily dissolved by organic solvents. Because oils difficult to purify were formed in most cases, dimethylmalonate was substituted for the ordinary ester and, as expected, solid addition products were obtained. The yields were not as good as with diethyl malonate, for greater difficulty was experienced in obtaining a complete reaction between sodium and the methyl ester.

These addition products behave exactly as one would expect of malonic ester derivatives. Complete decomposition is induced by heating with water containing either acid or alkali.

$$CH(COOC_2H_5)_2CSNHCH_3 + 4H_2O = CH_3COOH + 2CO_2 + H_2S + CH_3NH_2 + 2C_2H_5OH$$

With cold aqueous sodium hydroxide it is possible to obtain one of the intermediate products, malonic acid monothiomethylamide. It is formed as the result of the loss of carbon dioxide as well as hydrolysis.

$$CH(COOC_2H_5)_2CSNHCH_3 + 2H_2O = CH(COOH)_2CSNHCH_3$$
$$CH(COOH)_2CSNHCH_3 = CO_2 + CH_2(COOH)CSNHCH_3$$

These transformations take place at low temperatures and in alkaline solution, for hydrated sodium carbonate crystallizes out when concentrated solutions are used.

The substances actually isolated are not the free acids but sodium salts, although in the procedure first used the alkaline solutions of the thio-amides were decomposed with an excess of dilute hydrochloric acid. The fact that the sodium salts are alkaline toward phenolphthalein in water solution led to the discovery that sodium is present and not water of crystallization, an assumption that first suggested itself as the explanation of the low results observed on an examination of the analytical data for sulfur. The lower members of this series of salts are very soluble in water and quite insoluble in most organic solvents. Hence a very welcome observation was their solubility in acetone, which is an admirable vehicle for isolating them. It is not miscible in water containing alkali and so the sodium hydroxide solution of the thio-amides may be extracted directly with warm acetone. On cooling, the substances separate out as lustrous, irregular, plate-like crystals. The butyl and amyl derivatives are sufficiently sparingly soluble in cold water to permit the use of this solvent, although acetone is much the superior solvent. These salts are very hygroscopic and must be kept in a desiccator before analysis. Decomposition takes place on heating, with blackening and evolution of carbon dioxide. The free acids were not isolated, neither was the sodium salt of malonic acid monothiomethylamide, the first member of the series.

Malonic acid monothiobenzylamide, in marked contrast to the other amides, is precipitated from alkaline solution as the free acid by the addition of hydrochloric acid. It dissolves less readily in aqueous alkali than the other amides and is only sparingly soluble in water, from which it may be recrystallized. It loses carbon dioxide on heating, thereby changing smoothly into thio-acetyl benzylamide.

$$CH_2(COOH)CSNHCH_2C_6H_5 = CO_2 + CH_3CSNHCH_2C_6H_5$$

In this respect it acts like the corresponding derivatives obtained from the aromatic mustard oils. All of these sulfur derivatives have a bitter taste and react quickly with silver nitrate, forming silver sulfide.

Experimental

The mustard oils, except methyl and ethyl which can be purchased, were prepared by the method of Delépine,[2] in which a primary amine in water solution is brought in contact with carbon bisulfide and sodium hydroxide. Lead nitrate, substituted for lead acetate, was added to the mixture, which was then steam distilled. The yields of redistilled product varied from 50 to 75% of the theoretical. Sodium malonic ester was prepared in dry ether by the action of pulverized sodium. The preparation always contained metallic sodium even after long heating under a reflux condenser. Usually 10 g. of the ester was converted into the sodium derivative, after which the molar equivalent of the mustard oil was added and the mixture heated under a reflux condenser for several hours. The ester gradually changed into a heavy, compact white powder and the mixture showed a strong tendency to bump. It was then cooled and poured into water containing crushed ice. Any unchanged sodium present rose to the top and gradually disappeared in the moist ether layer without any danger of taking fire. Another advantage of having the ether present is that it extracts all organic impurities from the water layer except sodium malonic ester. The aqueous layer was then separated and acidified with an excess of dilute hydrochloric acid. An oil always formed but on standing for a few minutes it usually became solid. It was purified by dissolving in a small amount of warm alcohol and then adding water until the solution just missed becoming turbid.

The monothio-amides of malonic acid were obtained by dissolving the original addition product in 20% sodium hydroxide solution, using two or three times the equivalent amount of alkali and allowing the mixture to stand in a cool place overnight. Then by shaking with warm acetone and evaporating to a small bulk, the desired substance was quickly obtained in a relatively pure condition. The yields were only fair and an examination of the aqueous residue always revealed some of the original

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[2] Delépine, *Bull. soc. chim.*, [4] 3, 642 (1908).

thio-amide unchanged. Some hydrogen sulfide was also set free on the addition of a mineral acid, so it was evident that some of the material had entirely gone to pieces.

Malonic acid monothiobenzylamide was isolated by adding an excess of hydrochloric acid to the alkaline solution, filtering and recrystallizing the precipitate from warm water. In the analyses for sulfur the substances were heated to 225–250° for at least twenty hours with fuming nitric acid.

TABLE I

THIO-AMIDES

Of Carbethoxy Ethylmalonate

Name, Carbethoxy ethylmalonate monothio-	Formula	M. p., °C.	Decomp., °C.	Cryst. form	Sulfur analysis Calcd., %	Found, %
Methylamide	$C_9H_{15}O_4NS$	49–50	.....	Narrow plates	13.6	13.9
Ethylamide	$C_{10}H_{17}O_4NS$	51–52	.....	Needles	13.0	13.2
Propylamide[a]	$C_{11}H_{19}O_4NS$	11 (approx.)	.....	Needles	..	..
Butylamide[b]	$C_{12}H_{21}O_4NS$	Oil	.....	....	11.6	12.2
		Of Carbethoxy Methylmalonate				
Carbethoxy methylmalonate monothio-						
Propylamide	$C_9H_{15}O_4NS$	42–43	.....	Flat needles	13.8	14.1
Butylamide	$C_{10}H_{17}O_4NS$	62–63	.....	Needles	12.9	13.0
Amylamide	$C_{11}H_{19}O_4NS$	52–53	.....	Needles	12.2	12.5
		Of Malonic Acid				
Malonic acid monothio-						
Ethylamide	$C_5H_8O_2NSNa$	....	148–149	Plates	(Na, 13.6)	(Na, 13.4)
Propylamide	$C_6H_{10}O_2NSNa$	....	155–156	Plates	17.5	17.7
Butylamide	$C_7H_{12}O_2NSNa$	....	156–157	Plates	16.2	16.2
Amylamide	$C_8H_{14}O_2NSNa$	....	157–158	Plates	15.2	15.4
Benzylamide[c]	$C_{10}H_{11}O_2NS$	95–96	.....	Plates	15.3	15.3
		Of Acetic Acid				
Thio-acetyl benzylamide	$C_9H_{11}NS$	62–63	.....	Needles	19.4	19.5

[a] M. P. taken of crude subst. in water.

[b] Oil became crystalline in freezing mixture. Crude subst. analyzed.

[c] CO_2 evolved on melting.

Summary

Methyl, ethyl, propyl, butyl, amyl and benzyl mustard oils form addition products with sodium dimethyl and diethyl malonates.

These addition products in alkaline solution change into the sodium salts of malonic acid monothio-amides.

Under similar conditions the benzyl derivative forms the free acid. It loses carbon dioxide when heated to the melting point, changing into thio-acetylbenzylamide.

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