[CONTRIBUTION FROM THE BIOCHEMISTRY SECTION, MEDICAL DIVISION, ARMY CHEMICAL CENTER]

# THE CHEMICAL NATURE OF THE REACTION BETWEEN SULFUR AND CROTONIC ESTERS

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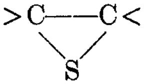
In 1895 Michael (1) described the addition of sulfur to ethylene compounds, namely the esters of crotonic and fumaric acid and styrene.[1] He formulated the resulting compounds as 3-membered rings, formed by the addition of one sulfur atom to the ethylene linkage: $>C{=}C< + S \rightarrow$  $>\underset{S}{C{-}{-}C}<$; on the other hand two molecules of ethyl acetylenedicarboxylate reacted with one sulfur atom to yield $\alpha,\alpha',\beta,\beta'$-tetracarbethoxythiophene.[2]

The assumption of the formation of ethylene sulfide derivatives in the experiments of Michael has been criticized by Westlake (5), since the compounds do not have any tendency to polymerize and after saponification by potassium hydroxide still contain sulfur. Westlake states: "In view of the sensitivity to various reagents, including alkali, which Delepine found ethylene sulfides of this structure to possess, and in view of the almost violent polymerization resulting therefrom, it is doubtful that the structure postulated by Michael was correct." However, up to now no other formulation for the mentioned products of sulfur addition has been given in the literature.

When we allowed sulfur to react with methyl crotonate without solvent at 180–190° according to the method of Michael, we obtained an oil of a reddish brown color and an unpleasant odor; b.p. 150–160°/1 mm. Michael gives b.p. 195–200°/30 mm. The sulfur content corresponds exactly to a ratio of one atom of sulfur *per* molecule of ester. However, both the color and the high boiling point are contradictory to the formulation of a simple monomolecular, 3-membered ring structure for the compound. Ebullioscopic determination of the molecular weight in benzene solution gave direct evidence that two molecules of methyl crotonate are contained in the addition product.

When the substance of Michael is stored at room temperature or at $-20°$ sulfur is deposited. Another sample split off sulfur upon slow distillation in a flask with a rectification column; a sulfur-rich, dark colored, tarry residue remained in the flask and a light yellow oil with a lower sulfur content distilled over. Further partial removal of sulfur may be attained by shaking a methanolic solution of the Michael compound with metallic mercury in excess.

One of the end products obtained by these manipulations had a sulfur content of exactly one mole sulfur *per* two moles of methyl crotonate. This is in favor of the assumption that this substance is a derivative of tetrahydrothiophene, and that in Michael's compound only one atom of sulfur is firmly bound.

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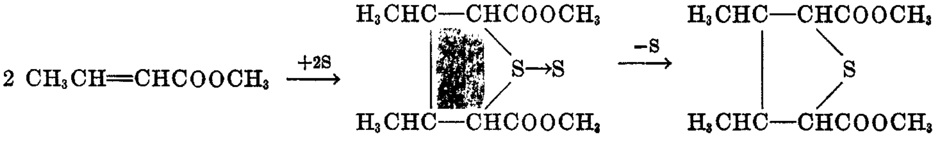
[1] The formation of a "disulfide" by the interaction between sulfur and cinnamic acid ester has been described (2). For the formation of "trithions," see (3).

[2] Examples of the formation of thiophene rings by the addition of sulfur to unsaturated aromatic compounds have been given recently by Russian authors (4).

The observed facts agree with the following formulation of the reaction:[3]



I II

It is assumed that the main product formed in the reaction is compound I; this formula is in agreement with the odor, color, boiling point, and molecular weight of the primary product of sulfur addition to methyl crotonate. Stabilization occurs with the splitting off of one sulfur atom, probably yielding compound II, which is a tetrahydrothiophene derivative. Because of the nature of compounds I and II, and the possible presence of several isomers, proof of the postulated reaction mechanism by independent synthesis appeared to be beyond the scope of the present study and must be left for future investigation.

By-products may be formed in the sulfur addition reaction, such as 6-membered disulfide structures and 1,4-dithiane derivatives.

*Influence of solvents.* The addition of sulfur to methyl crotonate takes place in boiling decalin in about the same manner as without solvent.

Boiling nitrobenzene is also a good solvent for sulfur. When we heated a mixture of nitrobenzene, sulfur, and methyl crotonate in a sealed tube slowly to 185° a very violent explosion resulted shortly after this temperature had been reached. In explanation of the explosive nature of this mixture it is assumed that product I is first formed. Sulfur in this form seems to be oxidized by nitrobenzene at a very rapid rate, as soon as a certain temperature is attained.[4] It was not possible to undertake the detailed investigation necessary to establish the reaction mechanism and to ascertain the theoretical or practical significance of the reaction.

In the reaction between sulfur and ethyl crotonate in boiling aniline the sulfur addition reaction is overshadowed to a considerable extent by a dehydrogenation process in which sulfur is removed as hydrogen sulfide. Two sulfur-free products could be isolated: a small quantity of *N,N'-diphenylurea* and a larger amount of a mixture of *ethyl anilinocrotonate* and *ethyl anilinobutyrate*. The genetic correlation between these types of compounds is given by the fact that diphenylurea is formed along with ethyl $\beta$-anilinocrotonate, when a mixture of aniline and acetoacetic ester is heated above 160° (8). In our experiment evidently the crotonate was reduced to some extent to a derivative of ethyl butyrate by reaction with hydrogen sulfide. The following equations might be formulated:

$$CH_3CH{=}CHCOOC_2H_5 + C_6H_5NH_2 + S \rightarrow CH_3C(HNC_6H_5){=}CHCOOC_2H_5 + H_2S$$

$$CH_3C(HNC_6H_5){=}CHCOOC_2H_5 + H_2S \rightarrow CH_3CH(HNC_6H_5)CH_2COOC_2H_5 + S$$

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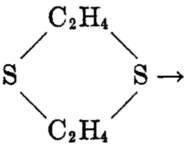
[3] The position of the methyl and carbomethoxyl groups in relation to the sulfur atoms is chosen arbitrarily.

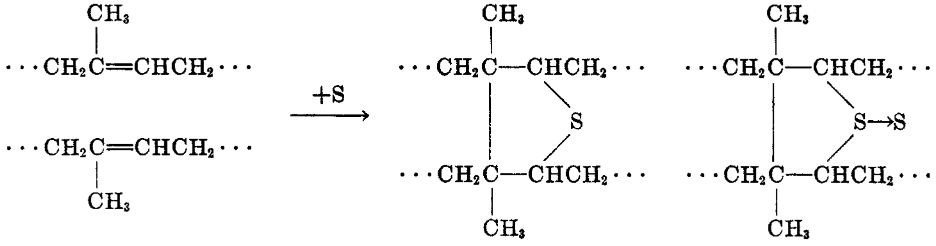
[4] For the interaction between sulfur and nitrobenzene at higher temperatures, see (7).

Whether the anilino-moiety enters only into the $\beta$-position, as formulated, or into the $\alpha$-position, or into both, is an open question.

We did not identify relatively small amounts of sulfur-containing products formed by the reaction of aniline, sulfur, and ethyl crotonate. Merz and Weith (9) were the first to observe a reaction between sulfur and boiling aniline to form "thioaniline." Hodgeson (10) has shown that the reaction product is mainly a mixture of bis(aminophenyl)sulfides and disulfides.

The explanation given here for the nature and structure of Michael's compound brings the addition of sulfur to the esters of crotonic acid and of acetylenedicarboxylic acid in harmony; in both cases thiophene derivatives are obtained. But whereas the primary sulfsulfide derivative ( $>S \rightarrow S$; analogous to a sulfoxide) seems to be stable in the tetrahydrothiophene series (crotonate + S), this should not be true for the thiophene series (acetylenedicarboxylic acid ester + S).

The formula I given in this paper for the Michael compound further conforms with Westlake's (6) formulation, , for the addition product of sulfur to ethylene. Furthermore, it is in accord with modern assumptions on the nature of the rubber vulcanization process. One possibility considered to be important for this is that the following reaction takes place, with the production of compound V (11):



V VI

Our results on the addition of sulfur to crotonic ester suggest the possibility that a primarily formed $>S \rightarrow S$ compound (formula VI) may be involved as an intermediate step in the vulcanization process.[5]

Furthermore, we suspect that the addition-product of sulfur to oleic acid as described by Rankoff (12) is the same type of bimolecular compound that we are discussing here. A corresponding derivative of elaidic acid (dithiane-elaidic acid) has been proved to be bimolecular also (13, 14).

It would appear therefore that no alkylene sulfide carboxylic acids have been

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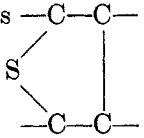
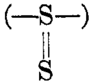
[5] Since the sulfur-methyl crotonate reaction product has the property of splitting off sulfur slowly, compounds of this type might well be tested for their usefulness in rubber vulcanization. The structural relationship between sulfur-vulcanized rubber and sulfurized methyl crotonate might favor the formation of solid solutions.

described up to now, contrary to the well known corresponding oxygen compounds, the epoxy fatty acids.[6]

*Addendum:* After this paper was submitted for publication the editors of the Journal of Organic Chemistry recalled to our attention the papers of Farmer, *et al.* (15), which might be of importance not only for the mode of addition of sulfur to olefins in general, but also for the special case treated in our paper. Farmer and coworkers found that hydrocarbons with one ethylene linkage (RH), when adding sulfur, yield dialkylpolysulfides of the general formula $RS_xR^1$, where R and $R^1$ appear on the average to be monoölefinic and saturated respectively ($R^1$ = dihydro R), and x was found up to 6. No ring forms such as  were observed with *monoölefins.*

It is possible that the addition of sulfur to crotonic esters gives similar aliphatic structures, because thus far no proof for a ring nature of the reaction products has been given.

Furthermore, Farmer's results show that conclusions concerning the structure of the polysulfide group ($S_x$) cannot be drawn from the lability of the sulfur, since linear sulfur chains (—S—S—S—S—) split off sulfur under certain conditions.

Therefore, although there may be some doubt that all the sulfur in the crotonic ester addition product described by us is present in the branched chain coordination form  $(-\underset{\underset{\displaystyle S}{\|}}{S}-)$ rather than in part as linear disulfide (—S—S—), we prefer the former explanation.

In spite of the remaining uncertainties the results presented in our paper can be considered to be a first step towards the elucidation of the true structure of the sulfur-crotonic ester addition product.

## EXPERIMENTAL

*A. Addition of sulfur to methyl crotonate, without solvent,* according to Michael (1). (a) A mixture of 24 grams of sulfur and 75 grams of methyl crotonate (1 atom of S *per* mole of crotonate) was heated to 180–190° for 40 hours, then fractionally distilled. The first fraction, b.p. 110–150° (~ 1 mm.), on dilution with a small amount of methanol and cooling to −20° gave crystals. These were washed with a small amount of petroleum ether and recrystallized twice from methanol; needles, m.p. 165–168°.

*Anal.* Found: C, 51.64; H, 5.33; S, 12.2; $CH_3O$, 29.5.

For saponification the substance was boiled with alcoholic potassium hydroxide for a

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[6] On samples of 9,10-epoxystearic acid and 1,10-epoxystearamide, for which we are indebted to Dr. Swern, Eastern Regional Research Laboratories, we found molecular weights in molten camphor (Rast) corresponding to the monomolecular formula. 9,10-Epoxystearic acid in benzene solution gave a melting point depression according to a molecular weight value of 528.2 (calc'd 300.5). This association is considered to be the same as observed in general for dissolved fatty acids at lower temperatures.

short time. A potassium salt precipitated, which was dissolved in water, and after acidification with mineral acid, the organic acid was extracted with ether, and crystallized three times from glacial acetic acid; m.p. (in a sealed capillary tube) 345° with decomposition (shrinking at 340°).

*Anal.* Found: C, 50.75; H, 4.98; S, 13.3; $CH_3O$, 1.2.

No special investigation on the purity and structure of the crystallized methyl ester and the acid was made. The ester seems to be formed by the union of two molecules of methyl crotonate and 1 atom of sulfur with cyclization and dehydrogenation. Oxygen and formaldehyde (formed by dehydrogenation of methanol) could be involved in the reaction too. The analysis of a similar product, including molecular weight determination, is given under (b).

The main product of reaction was a brownish-red (cherry colored) oil of disgusting odor; b.p. 150–160° (~ 1 mm.), after three times repeated fractional distillation.

*Anal.* Calc'd for $C_{10}H_{16}O_4S_2$: S, 24.24. Found: S, 24.20.

The alcoholic solution of the substance gave no color reaction with sodium nitroprusside in the presence of sodium carbonate. In diluted sodium hydroxide the typical sulfide color reaction occurred.

The oil was dissolved in alcohol and shaken with mercury. After filtration from mercuric sulfide over kaolin and removal of the solvent the remaining oil was distilled over iron wire in a high vacuum:

| B.P. (~1 mm.) | COLOR | SULFUR CONTENT, % |
|---|---|---|
| 80–100° | Light yellow-orange | 19.93 |
| (main product) 110–115° | Light yellow-orange | 18.33 |
| 130–140° | Dark yellow-orange | 20.63 |

(*b*) In a second run the mixture of sulfur and methyl crotonate was heated for a much shorter time, with the temperature being raised slowly from 140–185° during 2½ hours. There was a large amount of sulfur unchanged, indicating that the addition reaction was very incomplete.

The distillate, b.p. 110–160°/~ 1 mm., yielded as before a very small amount of crystals which after several recrystallizations from methanol melted at 165°. These were dried in a vacuum, over magnesium perchlorate, at 100°.

*Anal.* Found: C, 52.4; H, 5.3; S, 17.56, 18.6, 21.8; $CH_3O$, 24.5; Molecular weight, 220 (Rast).

The liquid portions were fractionally distilled repeatedly in a high vacuum. Between every distillation the fractions were stored at −20°; sulfur crystallized out and was eliminated mechanically. By this procedure the boiling point dropped lower and lower, to yield ultimately the following fractions:

| | B.P. (~0.1 mm.) | COLOR | ODOR | YIELD, ML. | SULFUR CONTENT, % |
|---|---|---|---|---|---|
| I | 86–88° | Orange-yellow | Not unpleasant | 4 | 15.01 |
| II | 88–113° | Orange-brown | Not unpleasant | 2.5 | 17.2 |
| III | 113–115° | Orange-brown | Sharp | 1.5 | 19.1 |
| IV | 137–165° | Orange-brown | Sharp | 2 | |

*Fraction IV.* The substance (2 g.) was treated with 10 ml. of 15% potassium hydroxide; after 12 hours at room temperature only a part of the material had dissolved. The dark red-brown solution gave a positive SH-test with sodium nitroprusside. After acidification with hydrochloric acid, hydrogen sulfide was evolved and colloidal sulfur was formed.

*Fraction II.*

*Anal.* Calc'd for 2 $C_{10}H_{16}O_4S$ + $C_{10}H_{16}O_4S_2$: S, 17.62; Average mol. wt., 232.8.
Found: S, 17.2; Mol. wt., 233.6 (cryoscopic in benzene).

It reacts with an aqueous solution of potassium permanganate with formation of manganese dioxide.

*Fraction I.* This portion was diluted with methanol and shaken with metallic mercury. After filtration and removal of the solvent, the residue was distilled in a high vacuum. Two fractions were collected.

| | B.P. (~1 mm.) | $n_D^t$ | COLOR | ODOR | ANALYSIS FOR $C_{10}H_{16}O_4S$ | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Calc'd | | | Found | | |
| | | | | | C | H | S | C | H | S |
| Ia | 110–120° | $1.4740^{25}$ | Yellowish Brown | Not unpleasant | — | — | 13.8 | — | — | 14.0 |
| Ib | 120–126° | $1.4744^{30}$ | | Not unpleasant (slightly onion-like) | 51.7 | 6.9 | — | 50.7 | 7.1 | — |

Ia heated with methyl iodide in a sealed tube for 3 hours at 100° yielded only a very small amount of crystals. Color reactions with sodium nitroprusside: Ia. In alcohol + $N/2$ sodium hydroxide (1:1); red-brown, after a short time, dirty brown-green; after a longer time pure green. In sodium carbonate solution no color reaction immediately; after a longer time dirty greenish-brown. Ib: In alcohol + $N/2$ sodium hydroxide (1:1) like Ia, but a little more intense.

*B. Addition of sulfur to methyl crotonate, in decalin.* Methyl crotonate (25 g.), 3.8 grams of sulfur, and 55 grams of decalin were sealed in a reaction bomb and heated at 182° for 48 hours. Distillation in a high vacuum yielded 10 grams of a yellowish-red liquid of unpleasant odor, b.p. 130–140° (~ 0.5 mm.). This was shaken in methanol with mercury for the removal of loosely bound sulfur. After distilling off the solvent the remaining liquid (5.7 grams) had $n_D^{26}$ 1.4805.

*C. Explosive reaction of sulfur, methyl crotonate, and nitrobenzene at 185°.* Methyl crotonate (24 g., b.p. 118–120°) and 8 grams of sulfur were refluxed with an air condenser in an oil-bath for several hours. During this operation a small amount of methyl crotonate escaped through the condenser; no sulfur was dissolved.

In order to raise the boiling point of the mixture, 25 ml. of nitrobenzene was added. The temperature of the oil-bath was kept at 165–175°; after 4 hours all of the sulfur was dissolved. No odor of sulfur dioxide or hydrogen sulfide could be detected, indicating that no reduction or oxidation of the sulfur had occurred. The boiling was continued for 4 more hours. The next day, all of the sulfur had crystallized out at room temperature indicating that no reaction had occurred.

To initiate a reaction it was decided to raise the temperature still higher. The mixture was sealed in a glass tube, surrounded by a heavy metal tube, and heated in an electric oven. After raising the temperature slowly from 140° to 185°, a very violent explosion took place approximately 3 minutes after the temperature was set at 185°, destroying not only the glass tube but also the whole front part of the hood in which the electric oven had been placed. The noise of detonation was not too loud but the explosion was accompanied by a large darting flame and a great pressure wave which spread over some yards in a horizontal direction through the door of the oven.

*D. Reaction of ethyl crotonate, aniline, and sulfur.* Ethyl crotonate, (30.2 g.), 4.8 grams of sulfur, and 60 ml. of aniline were refluxed for 16 hours. Much hydrogen sulfide was evolved. From the filtered mixture crystals deposited after cooling to room temperature. The crystals were thrice recrystallized from absolute methanol; weight, 0.4 grams; m.p. 235°. The literature gives m.p. 239° for N,N'-diphenylurea.

*Anal.* Calc'd for $C_{13}H_{12}N_2O$: C, 73.5; H, 5.6; N, 13.2.
Found: C, 73.6; H, 5.7; N, 13.0.

To the filtrate was added 4.8 g. of sulfur and refluxing was continued for a total of 40 hours. The resulting mixture was distilled *in vacuo* and two fractions were obtained:

| FRACTION | YIELD, G. | $n_D^{20}$ | B.P., °C. | MM. | ANALYSIS FOUND | |
|---|---|---|---|---|---|---|
| | | | | | N | S |
| I | 38.4 | 1.5623 | 53–54 | 3 | 13.2 | 0.65 |
| | | | 168 | 760 | | |
| II | 11.2 | 1.5245 | 138–140 | 3 | 6.7 | 2.29 |

Fraction I was converted to its hydrochloride which, after extraction with absolute ether (to remove impurities) had approximately the melting point of aniline hydrochloride. After liberation of the free base by potassium hydroxide the main fraction boiled at 183–184°; $n_D^{20}$ 1.5800 (literature value for aniline: b.p. 184°, $n_D^{20}$ 1.5863).

Fraction II was redistilled *in vacuo*; the main fraction (10 grams) boiled at 135–139° (~ 3 mm.). It was mixed with dry ether, and dry hydrogen chloride was bubbled through the solution. A hydrochloride precipitated in fairly good yield and was recrystallized from absolute ethanol; m.p. 170°. No sulfur was detectable. The aqueous solution of the hydrochloride gave a strong reaction with potassium permanganate, with formation of manganese dioxide.

*Anal.* Calc'd for $C_{12}H_{15}NO_2 \cdot HCl$: C, 59.6; H, 6.69; N, 5.8.
Calc'd for $C_{12}H_{17}NO_2 \cdot HCl$: C, 59.2; H, 7.45; N, 5.75.
Found: C, 59.3; H, 7.2; N, 5.7.

The analysis indicates that the mixed hydrochlorides of ethyl anilinocrotonate and ethyl anilinobutyrate were present. The mixture of free bases liberated from the hydrochlorides had $n_D^{20}$ 1.521, was insoluble in water, and yielded manganese dioxide with potassium permanganate solution.

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## SUMMARY

1. The addition product of sulfur and methyl or ethyl crotonate is not a three-membered ring compound as postulated in the literature. It has been shown that reaction takes place between two molecules of crotonic ester and two atoms of sulfur with the formation of either a sulfsulfide, derived from a substituted tetrahydrothiophene compound, or an aliphatic, disubstituted disulfide. One of the two sulfur atoms is split off rather easily.

2. Decalin as a solvent has no influence on the reaction. Nitrobenzene cannot be used as solvent; in the presence of this compound, at 185°, a violent explosion occurred. With aniline as solvent, the aniline, ethyl crotonate, and sulfur react with the evolution of hydrogen sulfide and formation of ethyl anilinocrotonate and ethyl anilinobutyrate, in addition to a relatively small amount of sulfur-containing compounds which have not been investigated.

3. The relation of the investigated reaction to similar ones is discussed.

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