[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

A STUDY OF THE REACTIONS OF SODIUM MALONIC ESTER.[1]

[SECOND PAPER.]

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In a previous paper[2] we have given experimental proofs of the existence of one of the addition compounds predicted by the theory of malonic ester reactions proposed by H. E. Bigelow and one of us[3] (but earlier by Von Findeisen[4]). In this paper we take up the remainder of our theory, and show that the course of the reaction depends in great measure on the relative attractions of the two parts of the substance added for the carbon attached to the sodium.

The theory may be briefly stated as follows: When an organic substance containing a halogen reacts with sodium malonic ester, the first stage is the addition of one atom of the halogen and the residual organic radical to the (enol) sodium malonic ester. If the halogen (X) has a greater attraction for the carbon carrying the sodium than the organic radical (R) has, it will be attached to it (I); and this will break up into sodium halide and substituted malonic ester. If, however, the organic radical (R) happens to have the stronger attraction for the carbon attached to the sodium, it will combine with this, giving the addition compound II, which will decompose into halogen malonic ester and either the sodium or hydrogen compound of the radical.

I. $C_2H_5OOC - RCH - CX(ONa)(OC_2H_5) = RCH(COOC_2H_5)_2 +$ NaX.

II. $C_2H_5OOC - XCH - CR(ONa)(OC_2H_5) = XCH(COOC_2H_5)_2 +$ RNa or RH, if the decomposition takes place on acidification.

The object of this paper is to study the conditions which cause the replacement of halogen by hydrogen (or sodium), under the influence of sodium malonic ester (II). According to our theory this takes place when the organic radical is more attracted than the halogen by the carbon carrying the NaO. In discussing Nef's theory of the hydrogen replacement[5] in our first paper, we brought forward as a grave objection to it the fact that it required the sodium to prefer the negative organic radical to the halogen. This objection does not apply to our theory, as according to it sodium itself does not attract the halogen or the organic radical, but an atom of carbon rendered positive by NaO, and in view of the fact

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[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy by Frank Clifford Whitmore.

[2] THIS JOURNAL, **37**, 1522 (1915).

[3] *Am. Chem. J.*, **46**, 549 (1911).

[4] *J. prakt. Chem.*, **65**, 530 (1902).

[5] *Ann.*, **308**, 306 (1899); *Am. Chem. J.*, **32**, 449 (1904).

that the attraction of carbon for halogen is not very strong at best, it seems not an unjustifiable supposition that this might prefer a strongly negative carbon atom to the halogen. Such a hypothesis, however, can be accepted only when supported by a large mass of evidence, and therefore in this paper we show that all the experimental results we have been able to find, are satisfactorily explained by our theory with a single exception—bromide of cyanogen—in which case sufficient data for a complete discussion are wanting.

The following list contains, we think, all the well-established cases, in which the halogen of an organic compound is replaced by hydrogen or sodium under the influence of a sodium ester.

Work in this laboratory has led to the discovery of the following cases, in which a halogen was replaced by hydrogen in nitrohalogen aromatic compounds. In this list the constitution of the substance is indicated by its formula, and the halogen replaced is printed in italics. The other reagent was sodium malonic ester, except where noted. $C_6NO_2BrHBrNO_2\mathit{Br}$,[1] also with sodium acetoacetic ester,[2] $C_6NO_2BrNO_2BrNO_2\mathit{Br}$,[3] $C_6NO_2BrBrBrNO_2\mathit{Br}$,[4] $C_6NO_2IHINO_2\mathit{I}$,[5] $C_6NO_2IBrINO_2\mathit{I}$[6] and perhaps $C_6HBrOH\mathit{Br}OHBr$,[7] although only the ethanetetracarboxylic ester could be detected in this case.

When, in beginning this study of our theory, we searched for halogen compounds with organic radicals negative enough to give the hydrogen replacement, the most promising seemed to be phenylsulfochloride, which, according to our theory, should give with sodium malonic ester, sodium phenylsulfinate and chloromalonic ester (or ethanetetracarboxylic ester). Upon looking up the literature, however, we found that this experiment had been tried already by Kohler and MacDonald[8] with *p*-tolylsulfochloride, and had given exactly the results predicted by us. Sodium acetoacetic ester also behaved in the same way (repeated later by von Findeisen[9]), and so did phenylsulfochloride and sodium camphocarboxylic ester as observed by Brühl.[10] We have also tried the action of phenylsulfochloride on sodium malonic ester with the formation of the sulfinate and ethanetetracarboxylic ester.

Closely related to these observations is the formation of sodium ethyl-

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[1] Jackson, Robinson, *Am. Chem. J.*, **11**, 93, 448 (1889).

[2] Jackson, Moore, *Ibid.*, **12**, 164, (1890).

[3] *Ibid*, **7**, (1890).

[4] Jackson, Bancroft, *Ibid.*, 289 (1890).

[5] Jackson, Langmaid, *Ibid.*, **32**, 297 (1904).

[6] Jackson, Bigelow, *Ibid.*, **46**, 549 (1911).

[7] Jackson, Dunlap, *Ibid.*, **18**, 111 (1896).

[8] *Ibid.*, **22**, 232 (1899).

[9] *J. prakt. Chem.*, **65**, 530 (1902).

[10] *Ber.*, **35**, 4113 (1902).

sulfite and ethanetetracarboxylic ester from ethylsulfuric chloride, C_2H_5-OSO_2Cl, observed by Willcox,[1] when sodium malonic ester was the other reagent. Sodium acetoacetic ester also gave the sulfite. Less closely related is Bischoff's[2] conversion of diethyldisulfonemethanediiodide, $(C_2H_5SO_2)_2CI_2$, into diethyldisulfonemethane with ethylenetetracarboxylic ester as the secondary product. The formation of the ethylene, instead of the ethane compound, is probably due to a secondary reaction. In all the cases so far mentioned the organic radical is strongly negative. In Kohler's[3] ethyl- and ethylenesulfocyanates, which gave with sodium acetoacetic ester disulfides (through the mercaptids), the organic radicals are less negative, but as in this case they are opposed to such a very weak negative radical as cyanogen, they might well take the position next the sodium. Kohler's interesting observation that the copper acetoacetic ester gave better results than the sodium salt may be caused by the fact that copper has a stronger attraction for sulfur than sodium has, as well as by the insolubility of the copper mercaptid. In continuation of this line of work we tried the action of 1-bromomercapto-2,4-dinitrobenzene, $C_6H_3(NO_2)_2SBr$, with sodium malonic ester, and obtained a little mercaptan and much disulfide, part of which may have been formed from mercaptan. In this case the attraction of the sulfur and phenyl for the positive carbon is reinforced by the two nitro groups, and thus may be made greater than that of the bromine.

Nef[4] has found that the 1^2-bromo- or iodophenylacetylene gave phenylacetylene and ethanetetracarboxylic ester with sodium malonic ester, and that sodium acetoacetic ester acted in the same way, while the chloro compound $C_6H_5C \equiv Cl$ gave a product derived from the union of the phenylacetylene radical with malonic ester. The well-known formation from acetylene of metallic derivatives (copper or sodium) indicates a strong attraction for positive radicals, which in this case, reinforced by phenyl, might well overcome the attraction of the bromine or iodine for the positive carbon, but not the stronger one of the chlorine.

In our own work on this subject we felt an especial interest in benzoyliodide, which, according to our theory, might give, with sodium malonic ester, benzaldehyd in addition to the benzoylmalonic ester—the sole organic product of the action with the chloride or bromide; and, in fact, our experiments yielded a substance showing many of the properties of benzaldehyd, but differing from it in such an important particular that its formation cannot be considered established without much more work, which unfortunately we were unable to give to it. This work, there-

[1] *Am. Chem. J.*, **32**, 474 (1904).

[2] *Ber.*, 30, 488 (1897).

[3] *Am. Chem. J.*, **22**, 68 (1899).

[4] *Ann.*, **308**, 305, 316, 321 (1899).

fore, is not used in the discussion of our theory. On the other hand, as we expected, nitrobenzoylchloride gave no aldehyd.

We have found also that bromomethanetricarboxylic ester, $BrC(COOC_2H_5)_3$, is converted into methanetricarboxylic ester by sodium malonic ester, and that α-bromodiphenylpropiophenone has the atom of bromine replaced by hydrogen.

While we were writing this paper we received an account of similar replacements of bromine by hydrogen in bromylphthalimide and bromylsuccinimide observed by Scheiber and Haun.[1] The reagents used were sodium malonic ester, or sodium cyanoacetic ester, and the same result was probably obtained with sodium acetoacetic ester, although in this case only the diacetosuccinic ester was detected.

The classes of compounds enumerated above have furnished 29 cases of the replacement of halogen by hydrogen (or sodium); and we can find only one thing which they have in common—all contain strongly negative radicals. Further, this negativity is produced in a great variety of ways: by nitrohalogenphenyl, oxygen compounds of sulfur, sulfur alone (in the sulfocyanates), or reinforced by nitrophenyl, phenylacetylene, carboxylester groups, phenylketones or imides of dibasic acids. This seems to us a very strong argument for our theory.

There remain to be considered only 10 cases of the replacement of halogen by hydrogen, in all of which the radical combined with the halogen is negative, but perhaps not enough so to be preferred to the halogen by the positive carbon. They belong in three classes: Reactions of substituted alkylmalonic esters, of polyhalides, and of bromide of cyanogen, and each will be discussed in detail.

Ruhemann[2] found that bromomethylmalonic ester and sodium malonic ester gave methylmalonic ester and ethylenetetracarboxylic ester,[3] and that the ethyl compound behaved in the same way. These results were confirmed by Bischoff,[4] who also extended them to the chloroesters, and added similar results from the action of chloro- or bromomalonic esters on sodium methyl- or ethylmalonic esters. Later in this introduction will be found a discussion of the radicals giving the hydrogen replacement, from which it appears that the malonic ester and alkylmalonic ester radicals are among the least negative that produce it. Taking Ruhemann's reaction of bromomethylmalonic ester as an example the theory would predict, therefore, that both the addition compounds III and IV would be formed, some molecules giving one, some the other, so that we should

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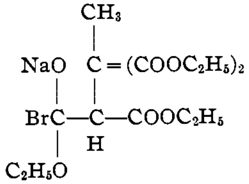
[1] *Ber.*, **47**, 3335 (1914).

[2] *Ibid.*, **26**, 2357 (1893).

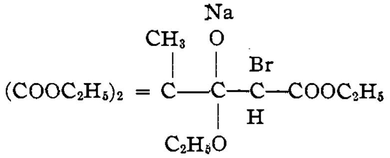
[3] We have shown that the formation of the ethylene ester is due to the use of heat. In the cold ethanetetracarboxylic ester is formed.

[4] *Ber.*, **29**, 1511 (1896).

expect a considerable yield of the substituted malonic ester formed from III,[1] and its comparative absence in the actual experiments needs explanation.



(III).



(IV).

The amounts formed of the two addition compounds (III) and (IV) will depend, in part, on the relative negativity of the halogen and organic radical, in part on the other conditions, and in every case will tend to reach an equilibrium; but they are so unstable that this equilibrium will be established between the products of their decomposition rather than between the addition compounds themselves. The decomposition of (IV) is represented by the following reaction:

$$(C_2H_5O)NaOC[CCH_3(COOC_2H_5)_2]CHBrCOOC_2H_5 = C(CH_3)[CONa(OC_2H_5)]COOC_2H_5 + CHBr(COOC_2H_5)_2,$$

that is, it falls into sodium methylmalonic ester and bromomalonic ester, but the latter will react at once with the excess of sodium malonic ester, since this reaction has been found to take place essentially instantaneously, whereas reactions involving alkylmalonic esters (whether bromo or sodium) are very sluggish. As soon, therefore, as the reaction has taken place, the bromomalonic ester will be converted into ethanetetracarboxylic ester, and the equilibrium being broken in this way, more of (IV) will be formed again and again in the effort to restore it, thus producing the large yield of ethanetetracarboxylic ester, while the substituted malonic ester produced from (III) will be reduced to a very small amount; and, as a matter of fact, Bischoff found that in all these experiments such minute quantities of the substituted malonic esters were obtained.

The other case where bromomalonic ester acts with sodium methylmalonic ester can be explained in the same way, but it is not necessary to give the details. On the other hand, we should explain why bromomalonic ester and sodium malonic ester give only the substituted malonic ester (in this case the ethanetetracarboxylic ester), whereas, since $—CH(COOC_2H_5)_2$ is more negative than $—CCH_3(COOC_2H_5)_2$, a greater amount of hydrogen replacement would be predicted. This is due to the fact that the addition product corresponding to (IV) can decompose only into the original reagents (bromomalonic ester and sodium malonic ester), so that

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[1] This would be especially the case with the chloro compounds.

here new products can be formed only by the addition corresponding to (III).

Two cases of replacement of halogen by hydrogen have been observed with polyhalides. Tetrachloride of carbon[1] gives with sodium malonic ester a derivative of chloroform and ethanetetracarboxylic ester; and tetraiodoethylene[2] gives acetylene and ethanetetracarboxylic ester. To explain the action of tetrachloride of carbon our theory requires that the radical CCl_3— should be more strongly attracted by the carbon carrying the sodium than free chlorine, which is certainly hard to believe; and yet the following considerations (if they are not too fanciful), justify this idea. The strong attraction for sodium residing in each atom of chlorine will be only partially neutralized by the union of the chlorine with carbon, for which it has much less attraction. It may be possible, therefore, that the residual attractions of the 3 atoms of chlorine left after union with the one atom of carbon should together exercise a stronger attraction for the positive carbon than the entire attraction of the single atom of free chlorine. This explanation would apply even better to the case of tetraiodoethylene, as it contains the less negative iodine.

Chloride of cyanogen gives cyanomalonic ester.[3] The bromide gives hydrocyanic acid and ethanetetracarboxylic ester.[4] At first sight this seems to be in accord with our theory as bromine should be replaced by hydrogen, when chlorine is not, but a more careful consideration shows this is not the case, because bromine is certainly more negative than cyanogen, and therefore the bromide should yield cyanomalonic ester instead of hydrocyanic acid. This is the only observation we have found, which is out of harmony with our theory. It may be caused by the intervention of other conditions, such as differences in solubility of the products, or of constitution in the cyanogen compounds, but at present not enough facts are known to decide whether this is the case. It is also possible that the effect of such other conditions may explain the reaction of tetrachloride of carbon rather than the theory proposed above.

We have considered now all the undoubted cases of hydrogen replacement, and have found only 1, bromide of cyanogen, which does not support our theory. In all these cases the hydrogen replacement was proved by the identification of its direct products. There are a few others, in which it can be inferred as an intermediate stage to interpret the actual results,[5] but in all these there may be other possible interpretations and so we prefer to omit them from our discussion, although they tell in our

[1] Dimroth, *Ber.*, **35**, 2881 (1902).

[2] Bischoff, *Ibid.*, **28**, 2832 (1895).

[3] Haller, *Ann. chim. phys.*, [6] **16**, 419 (1889).

[4] Nef, *Ann.*, **298**, 260 note (1897).

[5] Büchner, *Ibid.*, **284**, 223; Knovenagel, *Ber.*, **21**, 1355.

favor. We also leave out cases in which a ring is formed,[1] as this always introduces a disturbing condition, which may even prove to be the controlling one.

The foregoing discussion furnishes a strong argument in favor of our theory, as in every case of hydrogen replacement a distinctly negative organic radical takes part as was predicted, and it is further strengthened by considering the substances, which give the other—the malonic—replacement, as they on the whole are less negative. Thus the most negative substances which give this malonic replacement exclusively, are the acyl halides (except perhaps benzoyliodide), iodoanil, and benzalbromoacetophenone, to which should be added $BrC(COOC_2H_5)_2CH_2COOC_2H_5$ and $BrCCOOC_2H_5(CH_2COOC_2H_5)_2$, if these react normally, but there is good reason to think that in these cases the reaction consists in the removal of hydrobromic acid, followed by addition of malonic ester.

As, however, we have no strict method for the quantitative determination of negativity, so that it is in large measure a matter of judgment, a general comparison is less satisfactory than one confined to series of related substances, in which the negativity is produced by the same radical. The best case of this sort we have found is given in the following table:

$BrC(COOC_2H_5)_3$	Replacement by hydrogen only.
$BrCH(COOC_2H_5)_2$	Replacement by hydrogen with a little malonic ester.[2]
$BrCH_2(COOC_2H_5)$	Replacement by malonic ester only.

Here the nature of the reaction changes as the negativity of the radical decreases, exactly as predicted by our theory. Another similar case is the formation of a malonic ester derivative from chloroform, while in tetrachloride of carbon the fourth chlorine is replaced by hydrogen.

According to our theory the replacement of halogen by hydrogen is to be expected with bromine, iodine, or cyanogen, but only in exceptional cases with chlorine. As a matter of fact, of the 39 cases of this reaction known only 10 take place with chlorine compounds, and 5 of these are the exceptional cases anticipated, in which the radicals (containing sulfur and oxygen) associated with the chlorine are so negative that they may well be more strongly attracted by the positive carbon. The remaining 5, however—4 cases of chloromalonic esters and tetrachloride of carbon—are not directly in harmony with our theory, as their organic radicals belong to the least negative, with which such reactions have been observed. Our attempts to explain away these objections have been given already. A marked confirmation of the theory is found in Kohler's[3] work on the ethyl- and ethylenesulfocyanates, where but slightly negative radicals

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[1] For instance, Gutzeit, Engelmann, *J. prakt. chem.*, **66**, 123 (1902); Perkin, *J. Chem. Soc.*, **59**, 822 (1891).

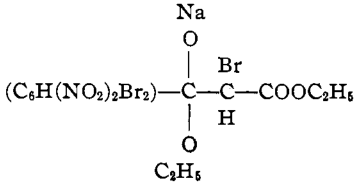
[2] When reacting with sodium methylmalonic ester.

[3] *Am. Chem. J.*, **22**, 68 (1899).

brought about the replacement by hydrogen, and this should be the case, when the halogen is cyanogen, the most feebly negative member of the group.

We would also call attention to the fact that our theory explains both the hydrogen replacement reactions and those in which substituted malonic esters are formed, whereas Nef used different theories[1] to explain these two sets of reactions.

Another strong point in favor of our theory is that it explains many complex chemical processes, which without it were decidedly obscure. For instance, 1,3,5-tribromo-2,4-dinitrobenzene with sodium malonic ester gives bromodinitrophenylmalonic ester,[2] the formation of which can be explained as follows: The first step would be the formation of the addition compound (V) because of the strongly negative character of the nitrobromo organic radical.

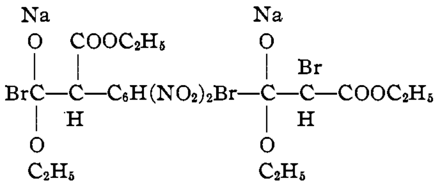


$$\begin{array}{rcccl}
 & \text{Na} & & & \\
 & \text{O} & & & \\
 & | & & \text{Br} & \\
(C_6H(NO_2)_2Br_2)— & C & — & C & —COOC_2H_5 \\
 & | & & \text{H} & \\
 & \text{O} & & & \\
 & C_2H_5 & & &
\end{array}$$

(V).

That this is the first stage of such reactions has been proved by the work of H. E. Bigelow and one of us on triiodobromodinitrobenzene.[3]

The addition compound (V) still contains a reactive atom of bromine, and therefore adds to a second molecule of sodium malonic ester, breaking for this purpose into bromine and [$C_6HBr(NO_2)_2C(ONaOC_2H_5)CHBr$-$COOC_2H_5$], but, as this complex radical contains an atom of sodium, its negativity will be so reduced that it will not be preferred to the bromine by the positive carbon, so the new addition compound will have the formula (VI).



$$\begin{array}{rcccccl}
 & \text{Na} & & & \text{Na} & & \\
 & \text{O} & COOC_2H_5 & & \text{O} & & \\
 & | & | & & | & \text{Br} & \\
\text{Br} & C & —C— & C_6H(NO_2)_2Br— & C & —C— & COOC_2H_5 \\
 & | & \text{H} & & | & \text{H} & \\
 & \text{O} & & & \text{O} & & \\
 & C_2H_5 & & & C_2H_5 & &
\end{array}$$

(VI).

This, on acidification, will yield sodium bromide, bromodinitrophenylmalonic ester, and bromomalonic ester (which could give ethanetetracarboxylic ester), the actual products of the reaction.

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[1] *Ann.*, **298**, 263 (1897); *Ibid.*, **308**, 306 (1899).

[2] Jackson, Robinson, *Am. Chem. J.*, **11**, 93 (1889).

[3] *Ibid.*, **46**, 549 (1911).

The fact that the third atom of bromine cannot be replaced either by hydrogen, or the malonic ester radical, is also explained by our theory. As is well known, bromine can be removed from the benzene ring only, when this is strongly negative, and in a compound like (VI) we should expect the two atoms of sodium to diminish the loosening effect of the two nitro groups, or even to destroy it, as was found to be the result here. If, however, there were three nitro groups present instead of two, we should not expect the reactivity of the last bromine to be completely destroyed by the two atoms of sodium, although it should be much diminished, and, as a fact, tribromotrinitrobenzene forms in the cold bromotrinitrophenylmalonic ester, in which the last bromine is retained; but if boiled with sodium malonic ester, this bromine also enters into reaction, and trinitrophenylenedimalonic ester is formed.

The explanation given above will not apply without modification to the behavior of triiodobromodinitrobenzene[1] which gives in the cold diiodobromodinitrobenzene, but this product, when heated with sodium malonic ester, forms iodobromodinitrophenylmalonic ester. Here the negativity of the organic radical cannot be reduced as in the preceding case, so a different way of converting the diiodobromodinitrobenzene into a sodium compound must be sought; and this is supplied by some work by Gazzolo and one of us,[2] which showed that sodium malonic ester combines with trinitrobenzene to form $C_6H_3(NO_2)_3[CHNa(COOC_2H_5)_2]_3$. The conformation necessary for such an addition was proved to be a nitro group in the ortho position to an atom of hydrogen or some other indifferent radical and, as in the diiodobromodinitrobenzene we have one such conformation, it seems certain that it will take up one molecule of sodium malonic ester, thus producing the reduction of its negativity required by our theory.

The formation of ethanetetracarboxylic ester in place of halogen malonic ester in many of our experiments needs some explanation, because the halogen malonic ester is not formed until the addition compound is destroyed by acidification, and it would seem this must destroy the sodium malonic ester necessary to form the tetracarboxylic ester; but, as a fact, in such cases the acidification took place by shaking the benzene solution with an aqueous acid, and was such a slow process that part of the sodium and halogen malonic esters had time to react on each other, before the whole of the former was destroyed.

An objection to our theory might be found in the speed with which the addition compounds leading to the hydrogen replacement are decomposed, since this action consists of the breaking apart of two atoms of carbon, which generally takes place less easily; but it is to be observed that both the

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[1] Jackson, Bigelow, *Am. Chem. J.*, **46**, 549 (1911).

[2] *Ibid.*, **23**, 388 (1900).

organic radicals are highly negative; and under these circumstances decomposition is often easy, as, for instance, in the decomposition of chloral by an alkali, and of hexabromodiacetyl, which is split by very weak alkaline reagents into bromoform and oxalic acid, while even water at 100° forms bromoform with it, according to observations made in this laboratory. The fact that one product of the decomposition is the very stable carboxethyl in our case would also make it take place more easily.

It might also be objected to our theory that it does not explain the reactions of sodium alcoholates with halogen nitro aromatic compounds, which give in some cases alkyl ethers, in others replacement of halogen by hydrogen, and therefore seem to be parallel to the reactions with sodium malonic ester. The absence of a double bond in these reagents makes it impossible to bring the cases directly under our theory, and we have found no modification of it that we feel able to accept, the formation of addition compounds containing quadrivalent oxygen, for instance, being contrary to all known analogy. If, then, the sodium alcoholate reactions are parallel to those with sodium malonic ester, they certainly involve an objection to our theory; but this relation between them is more apparent than real, as can be shown by a few differences. The phenylsulfochloride, if the reaction is parallel to that with sodium malonic ester, should give with sodium ethylate sodium sulfinate, whereas instead the product is phenylsulfonic ester. Tribromotrinitrobenzene also gives, with sodium malonic ester, bromotrinitrophenylmalonic ester, but with sodium ethylate a mixture of trinitrophloroglucineethylether and of tribromonitroresorcineethylether. It seems to us that these and similar differences justify the explanation of these sets of reactions by different theories, and therefore remove this possible objection to our theory, of the sodium malonic reactions.

Summary of the Evidence in Regard to the Theory.

1. One of the addition compounds predicted by it has been prepared in a pure state, and analyzed, as described in the first paper.
2. All the compounds, which give with sodium malonic ester the replacement of halogen by hydrogen, contain strongly negative radicals; those forming substituted malonic esters contain less negative radicals.
3. The replacement by hydrogen generally occurs with the less negative halogens—bromine, iodine or cyanogen. In the few cases in which chlorine is replaced by hydrogen, either it is associated with an exceptionally negative radical, or the action can be explained more or less satisfactorily by the intervention of other conditions.
4. The theory offers a satisfactory explanation of both classes of reactions.
5. It explains clearly complex organic processes, which without it were very obscure.

6. A possible objection that breaking apart two carbon atoms would not take place so easily as the decomposition of the addition compound leading to the hydrogen replacement was met by comparison with chloral and hexabromodiacetyl.

7. An objection that it does not explain the parallel reactions with sodium alcoholates was met by citing experiments to show that the two classes of reactions are really not parallel.

Experimental.

Action of Phenylsulfochloride on Sodium Malonic Ester.—In the introduction to this paper we have already mentioned the thorough work of Kohler and MacDonald[1] on the action of *p*-tolylsulfochloride on sodium malonic and acetoacetic esters. The action of phenylsulfochloride had not been tried, and, although this seemed hardly worth while, we thought an additional example of the hydrogen replacement would repay us for the slight amount of work involved. As we expected, we obtained sodium phenylsulfinate like Kohler and MacDonald, but unlike them, the product of the secondary reaction in our case was phenylsulfomalonic ester instead of the sulfoacetic ester obtained by them. This second product may be formed, as pointed out by Kohler and MacDonald, in two ways, either by some of the molecules of the sodium malonic ester giving the substituted malonic reaction, or by subsequent action between the sulfinate and the chloromalonic ester formed at first. That the second formation is the more probable they showed by carrying on this reaction between chloroacetoacetic ester and sodium *p*-tolylsulfinate, and in this case as in the primary reaction, obtained the *p*-tolylsulfoacetic ester instead of the acetoacetic ester;[2] whereas we, in a similar experiment with sodium phenylsulfinate and chloromalonic ester, obtained phenylsulfomalonic ester. These two differences between the results of Kohler and MacDonald, on the one hand, and ours, on the other, are obviously due to differences in the treatment. In the sulfochloride reaction the substituted malonic ester formed at first may have been decomposed because they dissolved it in water, and then evaporated the solution to dryness, whereas our product was made in the cold, and without exposing it to water. On the other hand, in their chloroacetoacetic ester experiment the use of heat and water was avoided, so that here we can only suggest the standing for two weeks, as the cause of the conversion of the acetoacetic ester into the acetic ester, since, in our work, the reacting mixture was not allowed to stand, but was worked up at once.

Kohler and MacDonald in one of their experiments obtained from the tolylsulfochloride and sodium acetoacetic ester 70% of sulfinate and 22% of tolylsulfoacetic ester. These yields are explained by the precipitation

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[1] *Am. Chem. J.*, **22**, 232 (1899).

[2] This had been tried earlier by Otto, *Ber.*, **23**, 736 (1900).

of the sodium sulfinate by the ether used in the solvent, thus removing it from the sphere of the reaction as fast as it was formed. The account of our own work follows:

Sodium malonic ester prepared from the sodium ethylate from 3.5 g. of sodium and 28 cc. of malonic ester, diluted with several volumes of ether, was treated with phenylsulfochloride diluted with 20 cc. of dry benzene and the same volume of dry ether. A heavy, white precipitate formed at once, but in order to be sure the reaction was complete, the mixture was allowed to stand in the cold for 10 days, during which time the sodium ethylate from about 3.5 g. of sodium was added gradually, until the odor of the sulfochloride had gone. The precipitate was then filtered out, and washed with several small portions of ether. As the washings evaporated, long, white needles were deposited which were proved to be ethanetetracarboxylic ester by the melting point 75° (uncor.) instead of 76°, as this was not altered, when the specimen was mixed with one of known ethanetetracarboxylic ester.

The white precipitate was heated for some time with absolute alcohol, and filtered hot, when the filtrate on cooling deposited a considerable amount of white microscopic rectangular plates, while different crystals were obtained from the filtrate, after it had been evaporated to a small volume. The rectangular plates nearly insoluble in cold absolute alcohol were dissolved in water, and treated with hydrochloric acid, when a white, cloudy precipitate was obtained, but without filtration the mixture was extracted with ether, which yielded crystals melting at 83° (uncor.) after one crystallization from hot water. Phenylsulfinic acid melts at 83–84°. Both the acid and its sodium salt gave a characteristic white, flocculent silver salt soluble in nitric acid or in ammonium hydroxide. There is no doubt, therefore, that the substance is sodium phenylsulfinate.

The salt soluble in cold absolute alcohol gave on analysis

Subs., 1.0463; Na_2SO_4, 0.2533.
Calc. for $C_6H_5SO_2CNa(CO_2C_2H_5)_2$: Na, 7.14; found: Na, 7.84.

The salt is therefore the sodium phenylsulfomalonic ester, the somewhat high result being due to some sulfinate which had been separated from it only by one crystallization from absolute alcohol. The sodium salt of phenylsulfoacetic ester contains 9.20% of Na.

Action of Chloromalonic Ester on Sodium Phenylsulfinate.—When solutions of equivalent amounts of the two substances in absolute methyl alcohol were mixed, a heavy, white precipitate of sodium chloride was formed at once. The filtrate was treated with a solution of sodium hydroxide in absolute methyl alcohol, until barely alkaline to phenolphthalein, and then on evaporation furnished white crystals, which were analyzed without purification.

Subs., 0.6035; Na_2SO_4, 0.1397.
Calc. for $C_6H_5SO_2CNa(COOC_2H_5)$: Na, 7.14; found: Na, 7.50.

The products of the reaction, therefore, are phenylsulfomalonic ester and sodium chloride.

Action of Sodium Malonic Ester on 1-Bromomercapto-2,4-dinitrobenzene.—The 1-bromo-2,4-dinitrobenzene (melting at 71° (uncor.), instead of 72°), was converted into 2,4-dinitrophenyldisulfide, which blackened at 245° and melted at 285°, and this is as near as can be expected to its decomposition point, given as 280°. A specimen of this suspended in carbon tetrachloride was mixed with bromine in the proportion of one molecule of each substance. In a short time the color of the bromine had nearly disappeared, when the precipitate was washed with carbon tetrachloride. As it was essentially insoluble in all organic solvents, we saw no means of purifying it, and therefore used it direct in our experiments, although an analysis gave 21.94% of bromine instead of 28.67 calculated for the bromomercaptan, showing that it contained a quantity of unchanged disulfide. It blackened at about 120° instead of at 245°, as it should if the disulfide, and was proved to be the bromomercaptan by boiling a little of it with water, when the filtrate gave a strong test for hydrobromic acid with silver nitrate. A purer product was obtained by longer standing with the bromine and greater care in drying the carbon tetrachloride, but too late for our experiments.

Sodium malonic ester was prepared by the action of sodium on malonic ester in ether, which had been carefully dried but not previously freed from alcohol, and mixed with 1-bromomercapto-2,4-dinitrobenzene, suspended in benzene in the proportion of one molecule of the latter to 2 of the former. The mixture turned red, and most of the solid went into solution, showing that a reaction had taken place, as the bromomercaptan is insoluble in all the solvents present. After standing two days the red color had changed to pale yellow, and a heavy precipitate had formed. The filtrate from this was shaken with dilute sulfuric acid, and on evaporation yielded a small quantity of yellow crystals, which melted at 130° (uncor.), after crystallization from a mixture of ether and alcohol;—1-mercapto-2,4-dinitrobenzene melts at 131°. The crystals dissolved in dilute sodium hydroxide, and were reprecipitated unaltered on acidification. There seems to be no doubt, therefore, that they were the mercaptan. We were unable to analyze our specimen at the time we made it, and when the opportunity came, it had decomposed, as shown by a rise of over 50° in the melting point, undoubtedly due to the partial conversion of the mercaptan into the disulfide.

The precipitate was extracted with various solvents in the hope of obtaining more of the mercaptan and the expected ethanetetracarboxylic ester, but the oils obtained deposited no crystals even after standing for

6 months, so we have no evidence of the formation of the tetracarboxylic ester. The undissolved portion of the precipitate was essentially insoluble in all solvents, and we suppose it to be mostly 2,4-dinitrophenyldisulfide, although it melted in the neighborhood of 260° with decomposition instead of at 280°. We have not thought it worth while to try to determine the nature of this body more accurately, since, as already noted, our bromomercaptan contained an impurity of the disulfide, so that its presence cannot be used as a proof of the formation of the mercaptan, although there is no question much of the mercaptan would have been converted into it both by the action of unchanged bromomercaptan and by the oxidizing action of the air.

Benzoyliodide and Sodium Malonic Ester.—This action was studied, because, according to our theory, benzoyliodide might give, with sodium malonic ester, benzaldehyd in addition to benzoylmalonic ester, the only product obtained with the chloride and bromide, which contain more negative halogens, and although our experiments could not be brought to a definite conclusion, owing to lack of time, it seems worth while to give a brief account of them.

The benzoyliodide was prepared by the excellent method of Staudinger and Anthes,[1] consisting in the treatment of benzoylchloride with carefully dried hydriodic acid. They give no directions for drying the acid, and, as we found this not altogether simple, we give the results of our experience. At first we used phosphoric pentoxide tubes alone, but found they were incapacitated so quickly by the iodine present that we adopted instead the following arrangement, which proved satisfactory: The hydriodic acid made from iodine red phosphorus and water was passed through a trap consisting of a long slender bottle lying horizontally, which kept back most of the iodine; then through 3 tubes of phosphoric pentoxide, followed by a U-tube immersed in ice and calcium chloride and standing in a Dewar flask. This removed the last trace of the iodine, after which the gas passed through freshly distilled benzoylchloride in a flask protected from moisture by a phosphoric pentoxide tube. The action was continued until a solution of the issuing gas gave no test for hydrochloric acid. The benzoyliodide prepared in this way was colorless, but on exposure to the light soon turned brown from liberation of iodine. For this reason the flask containing the benzoylchloride was carefully screened from light throughout the operation, and the product was used at once, after having been freed from the excess of hydriodic acid by a stream of dry carbonic dioxide. As the presence of iodine would interfere with our experiment by forming ethanetetracarboxylic ester, we used only fresh, colorless specimens, thinking that this was safer than trying to remove the iodine from altered

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[1] *Ber.*, 46, 1417 (1913).

specimens by means of mercury, as recommended by Staudinger and Anthes.

After treatment with sodium malonic ester the benzoyliodide gave as the principal product benzoylmalonic ester, but if the oil containing this was shaken with warm water, and the solution thus obtained mixed with an equal volume of glacial acetic acid, and treated with phenylhydrazine, a small quantity of solid was obtained, which, after crystallization from hot alcohol, showed the constant melting point 163° (uncor.). It was divided into 4 fractions by partial precipitation of the alcohol solution with water, all of which melted at 163° (uncor.), so that it seemed to be homogeneous. Benzylidenephenylhydrazone prepared from benzaldehyd in the same way melted at 158° (uncor.), and when mixed with our product melting at 163°, the mixture melted at 160° (uncor.). On the other hand, benzoylphenylhydrazid prepared from fresh benzoyliodide and phenylhydrazine and melting at 167° (uncor.), instead of 168°, gave with our product melting at 163° a mixture melting at 135–140°. This is strong evidence that benzaldehyd was present in the product from the action of benzoyliodide on sodium malonic ester, but it cannot be accepted without much more work, because the melting point of our product does not agree with that of benzylidenephenylhydrazone. It is, in fact, 7° higher than the one usually accepted—156°, Behrend and Leuchs.[1] There is, however, some evidence that this melting point is too low. Reutt and Pawlewski[2] found 158-160°; and in the last edition of Richter's Lexicon it is given as 160°, but we have been unable to find whether this is founded on Reutt and Pawlewski's work, or is independent of it. The benzylidenephenylhydrazone prepared from benzaldehyd by our process also melts higher—at 158° (uncor.), so that more study of this melting point seems desirable, but even if the true melting point should prove to be 160°, it is still 3° below that of the product from benzoyliodide, and this discrepancy has prevented us from using this work in the discussion of our theory. We regret that the pressure of other researches has prevented us from giving further study to this subject. We could find no ethanetetracarboxylic ester among the products, but a small amount of it remaining dissolved in the oil would have escaped identification.

Action of *p*-Nitrobenzoylchloride on Sodium Malonic Ester, $C_6H_4NO_2$-$COCH(COOC_2H_5)_2$.—Five g. of the chloride made from *p*-nitrobenzoic acid melting at 235° (uncor.), instead of 238° were mixed with 4.5 g. of malonic ester dissolved in dry ether, and the mixture was treated with an absolute alcohol solution of the sodium ethylate from 0.5 g. of sodium. A heavy, white precipitate formed at once, but, to complete the reaction, the mixture was allowed to stand for 4 days, after which the filtrate was

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[1] *Ann.*, **257**, 227.

[2] *Chem. Zentr.*, **1903**, II, 1432.

shaken with dilute sulfuric acid, and allowed to evaporate. White needles were obtained in this way, which, after washing with a sodium carbonate solution, were recrystallized from hot methyl alcohol, until they showed the constant melting point 93° (uncor.). No *p*-nitrobenzaldehyd or ethanetetracarboxylic ester could be detected among the products of the reaction.

Subs., 0.2941; N_2, 11.8 cc. at 18° and 765 mm.
Calc. for $C_6H_4NO_2COCH(COOC_2H_5)_2$: N, 4.53; found: N, 4.66.

Properties of *p*-Nitrobenzoylmalonic Ester.—It forms white needles from methyl alcohol, which melt at 93° (uncor.). It is easily soluble in ethyl alcohol, ether, chloroform, or acetone; slightly soluble in cold methyl alcohol, or ethyl acetate, easily soluble hot; essentially insoluble in water.

Action of Bromomethanetricarboxylic Ester on Sodium Malonic Ester.—The methanetricarboxylic ester used by us boiled between 140° and 143° at 20 mm., and was, therefore, essentially pure. It was mixed with bromine in the proportion of one molecule of each, and, as at first no action took place, the mixture was warmed on the steam bath, which started a vigorous reaction. This was controlled by cooling with running water or warming, until the color of the bromine had disappeared, when it was shaken with powdered sodium carbonate, and allowed to stand with it over night. In the morning its reaction was neutral, and it was distilled under diminished pressure, the fraction boiling at 168–170° at 20 mm. being retained for use.

Eleven grams of this bromomethanetricarboxylic ester were mixed with the sodium malonic ester from 12 g. of the ester and 1.6 g. of sodium in dry ether and benzene, that is, two molecules of the sodium malonic ester for each molecule of the bromine compound. The mixture, after standing for nine weeks, was filtered from the precipitate of sodium bromide, and shaken with 10 cc. of strong hydrochloric acid diluted with 100 cc. of water, the benzene layer washed with dilute sodium carbonate solution, and dried over calcium chloride. On evaporating off the solvents an oil was obtained, which soon deposited crystals identified as ethanetetracarboxylic ester by the melting point, which was unchanged when mixed with a quantity of the pure ester. The oil obtained from the mother liquors and drained from the crystals came over for the most part between 170° and 175° at 45 mm. Methanetricarboxylic ester should boil at about 172° at this pressure, and, as this fraction gave no test for bromine, there seems no doubt that it was the methanetricarboxylic ester. After this fraction had passed over, the temperature rose to 270°, and the distillate obtained crystallized on cooling, and was recognized as ethanetetracarboxylic ester by its melting point. The pure crystals of this substance from the original oil weighed 7.5 g., that is, 67% of the calculated amount. This yield would be somewhat increased by the amounts obtained from the mother liquors and the higher fraction. Apparently no other products were formed.

Action of α-Bromodiphenylpropiophenone with Sodium Malonic Ester.—This substance was prepared by the action of bromine on the saturated ketone obtained from benzalacetophenone and phenylmagnesium bromide. Sodium malonic ester was prepared by treating 8.8 g. of malonic ester with the sodium ethylate prepared from 1.27 g. of sodium. The amount of absolute alcohol was kept so low that the whole solidified. To this was then added 10 g. of the bromine compound dissolved in dry benzene. The proportion, therefore, was 2 molecules of the ester to each molecule of other reagent. The sodium malonic ester dissolved giving an orange solution, which, after the mixture had stood 2 hours, had deposited a heavy, white precipitate, but in order to be sure the reaction had run to an end, it was allowed to stand 3 weeks. The product was shaken out with dilute sulfuric acid, when the benzene layer on evaporation left an oil, which solidified on stirring. The white solid thus obtained after several crystallizations from alcohol melted at 93° (uncor.), instead of at 95°, the melting point of the ketone $(C_6H_5)_2CHCH_2COC_6H_5$ but, as a mixture of our product with the pure ketone melted at 93–94°, there can be no doubt it is this compound. The yield of substance melting at 93° was 6 g., that is, 76% of the theoretical, and, as this had been crystallized several times, the reaction for its formation must have run essentially quantitatively. The mother liquors from these crystals on concentration and standing over night yielded other crystals, which, after purification from hot ether, proved to be ethanetetracarboxylic ester, of which 4.7 g. were obtained, that is, 54% of the theoretical yield, but this comparatively small amount was explained by obtaining from the mother liquor 2.5 g. of an oil, which was principally bromomalonic ester to judge from its smell.

Mr. J. B. Conant, of this laboratory, informs us that, when he treated α-bromo-3-bromo-4-methoxyphenylpropiophenone, $CH_3OC_6H_3BrCH_2$-$CHBrCOC_6H_5$, with sodium malonic methylester, he obtained a small amount of the ethanetetracarboxylic methylester, indicating a similar reaction in this case, although apparently a less complete one than with the substance studied by us.

Reactions with Derivatives of Methylmalonic Ester.—In his work on these compounds Bischoff[1] found that chlorine compounds gave, as a rule, ethanetetracarboxylic ester, while the bromine compounds yielded ethylenetetracarboxylic ester. In only one case did he obtain the ethane ether from a bromine compound (bromomalonic ester with sodium methylmalonic ester), and then it was mixed with the ethylene compound. On the other hand, the chlorine compounds could be made to yield the ethylene ester by carrying on the reaction in boiling xylene. This result suggested

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[1] *Ber.*, **29**, 1510, 1515 (1896).

the idea that the ethylene derivative owed its formation to the action of heat, but, as it was possible that instead its appearance indicated a different course of the reaction, we have repeated Bischoff's experiments with bromine and methyl compounds carrying on the work in the cold.

Five grams of bromomethylmalonic ester diluted with its own volume of dry benzene were added to a dry benzene solution of 15.8 g. of malonic ester previously treated with the sodium ethylate from 2.2 g. of sodium. After standing in the cold 3 weeks the product was shaken with dilute hydrochloric acid, and the benzene layer allowed to evaporate spontaneously, when it yielded 4.3 g. of ethanetetracarboxylic ester, that is, 68% of the theory. We could find no trace of ethylenetetracarboxylic ester, but there may have been some of it dissolved in the oil. In this case, however, the large yield of the ethane compound shows that the ethylene derivative could not have been formed in large quantity.

Five grams of methylmalonic ester and the sodium ethylate from 0.66 g. of sodium were dissolved in dry benzene, and added gradually to 34.3 g. of bromomalonic ester also dissolved in dry benzene. After standing in the cold for 3 weeks the product was worked up as in the previous experiment, yielding an oil, which deposited 0.9 g. of ethanetetracarboxylic ester. This small yield was undoubtedly due to the solution of most of the product in the oil consisting of the excess of bromomalonic ester. No ethylenetetracarboxylic ester was detected, and while it is possible that some of it was present in the oil, it could not have been the principal product, as in that case the crystals would have contained some of it.

It follows from our experiments that ethanetetracarboxylic ester is the product, if the work is carried on in the cold, and that therefore the ethylenetetracarboxylic ester obtained by Bischoff owed its origin to the fact that his preparations were carried on at the boiling point of absolute alcohol, or at that of xylene.

Although the action of picrylchloride on sodium malonic ester has been frequently studied[1] in this laboratory, and careful search has been made for trinitrobenzene in the reaction products, no trace of this substance has been detected, so that the reaction runs principally, if not exclusively, in the usual way. In the hope of a different result we have tried the action of picrylchloride on sodium methylmalonic ester, but could find no trace of trinitrobenzene or dimethylethanetetracarboxylic ester. The principal product crystallized in flat straw-colored needles, and melted constant at 78–79°. We have no doubt that it was the trinitrophenylmethylmalonic ester, but it was so explosive that we did not succeed in getting a good analysis of it, and as the main object of this experiment had been obtained, we did not feel inclined to use up on a secondary point the large

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[1] Jackson, Soch, *Am. Chem. J.*, 18, 133 (1896); Jackson, Phinney, *Ibid.*, 21, 418 (1899).

amount of time, which would have been necessary to establish the composition of this substance.

The action of sodium malonic ester was also tried with the following substances: Nitro- and dinitrobenzyliodide, and the corresponding sulfocyanates, triiodoresorcine and tetrabromoorthoquinone; but in each case the product was an unmanageable oil, from which our greatest efforts failed to isolate any definite compound. Diiodoacetylene gave no reaction with sodium malonic ester, whether the solvent was absolute alcohol, dry ether, or dry benzene. We add a few observations made in the course of this work.

p-Nitrobenzylsulfocyanate, $C_6H_4NO_2CH_2SCN$.—This substance was prepared by Henry[1] in 1869, but, as he does not even give the melting point of it, we describe it more in detail. *p*-Nitrobenzylchloride was mixed with potassium sulfocyanate in acetone solution, and the filtrate from the potassium chloride, which precipitated at once, was washed with water and cooled alcohol, after which the residue was recrystallized from hot alcohol, until it showed the constant melting point, 85–86° (uncor.).

Subs., 0.2368; $BaSO_4$, 0.2863.
Calc. for $C_6H_4NO_2CH_2SCN$: S, 16.58; found, S, 16.61.

Properties of p-Nitrobenzylsulfocyanate.—It forms very pale yellowish, long needles or slender prisms, which melt at 85–86° (uncor.), and dissolve easily in acetone, chloroform, or ethylacetate; soluble in benzene; slightly soluble in cold, soluble in hot alcohol, methyl alcohol, or ether; soluble in cold, very soluble in hot glacial acetic acid; almost insoluble in cold, soluble in hot carbon tetrachloride; slightly soluble in carbon disulfide; insoluble in cold, slightly soluble in hot petroleum ether; insoluble in water.

2,4-Dinitrobenzylsulfocyanate, $C_6H_3(NO_2)_2CH_2SCN$.—This substance was prepared in the same way as the mononitro compound. It showed the constant melting point, 86–87° (uncor.). It is certainly strange that this should differ by only one degree, from the melting point (85–86°) of the mononitro compound. A mixture of the two melted at 58–60°.

Subs., 0.2390; $BaSO_4$, 0.2342.
Calc. for $C_6H_3(NO_2)_2CH_2SCN$: S, 13.39; found: S, 13.46.

Properties of 2,4-Dinitrobenzylsulfocyanate.—It forms pale yellowish, short prisms terminated at both ends by planes at a somewhat acute angle. It melts at 86-87° (uncor.). It is very soluble in acetone, chloroform, or ethyl acetate; soluble in benzene; slightly soluble in the cold, soluble hot in alcohol, methyl alcohol, or glacial acetic acid; slightly soluble in ether, or carbon disulfide; almost insoluble cold, slightly soluble hot in carbon tetrachloride; essentially insoluble in petroleum ether, or water. In general, it is slightly less soluble than the mononitro compound.

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[1] *Ber.*, **2**, 638 (1869).

The best solvent for it is hot alcohol. Both these sulfocyanates should be handled with care, as they have an irritating action on the skin, which in extreme cases may cause serious poisoning.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY.]

STUDIES IN ESTERIFICATION. VI. THE ESTERIFICATION OF BENZOIC ACID BY MERCAPTANS.

BY L. S. PRATT AND E. EMMET REID.

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Introduction.

A study of the elements in any group of the periodic system reveals certain analogies and certain contrasts in their behavior. Both analogies and contrasts are found when we compare organic oxygen and sulfur derivatives.

One of the most studied organic reactions is that of esterification, while but little attention has been devoted to the esterification of any but oxygen alcohols.

The study of the esterification of sulfur alcohols was taken up in the hope of throwing light on the theory of esterification, and of comparing mercaptans, or sulfur alcohols, with oxygen alcohols.

Historical.

The classical experiments of Berthelot and Péan de St. Gilles,[1] and the more exact work of Menschutkin[2] and Lichty[3] have shown that, when an alcohol is heated with an acid, esterification takes place and a well-defined limit is reached, and that the same limit may be reached by heating the corresponding ester with water.

$$(1)\ CH_3COOH + HOC_2H_5 \rightleftarrows CH_3COOC_2H_5 + HOH.$$

The following values from the work of Menschutkin[4] show the limits obtained by heating acetic acid and alcohols in equimolecular quantities, at 154°:

Methyl	69.52
Ethyl	66.57
Propyl	66.85
n-Butyl	67.30
iso-Butyl	67.38
Octyl	72.34
Cetyl	80.39

If these results are plotted as a curve, ethyl alcohol is found at the minimum, the limits increasing gradually with the molecular weights

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[1] *Am. Chem. Pharm.*, [3] **65**, 385–422 (1862); **66**, 5–218 (1862); **68**, 225–359 (1863).

[2] *Ber.*, **11**, 1507 (1878); **10**, 1728 (1877).

[3] *Am. Chem. J.*, **17**, 27 (1895); **18**, 590 (1896).

[4] *Ber.* **11**, 1510 (1878).