[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD UNIVERSITY.]

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

[FIRST PAPER.]

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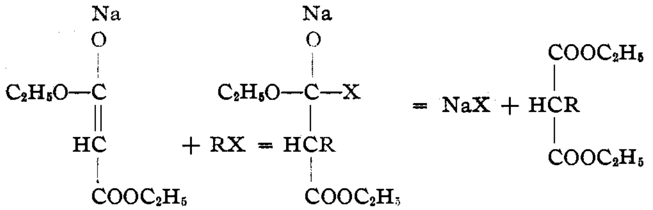
This paper contains a proof that the first step in the reaction of sodium malonic ester and an organic halogen derivative consists in the union of the two reagents to form an addition compound. It therefore places on a firm experimental basis that part of the theory proposed recently by Bigelow and one of us to explain these reactions; but it has also a wider interest, since it increases by one the meagre list of such intermediate compounds, and thus adds weight to the common theory that substitution is preceded by addition.

In 1888 W. S. Robinson and one of us[2] found that when sodium malonic ester reacted with tribromodinitrobenzene one of the atoms of bromine was replaced by hydrogen and one by the malonic ester residue, while the third remained unaltered, giving bromodinitrophenylmalonic ester. Further work in this laboratory led to the discovery of other cases of this strange replacement of a halogen by hydrogen, but no progress was made toward explaining the reaction until 1911, when H. E. Bigelow and one of us[3] found that bromotriiododinitrobenzene was converted by sodium malonic ester in the cold into bromodiiododinitrobenzene, but, if the reagents were heated, that bromoiododinitrophenylmalonic ester was formed. These experiments showed that the replacement of halogen by hydrogen preceded that by the malonic ester radical, and led to the following explanation[3] of the reactions with sodium malonic ester: When an organic substance containing a halogen reacts with sodium malonic ester, the first step consists in the addition of the halogen and the organic radical to the (enol) sodium malonic ester. Owing to the attraction of the sodium, the more negative part of the compound will be added to the carbon atom carrying the NaO. As a rule this would be the halogen



$$\begin{array}{c} \mathrm{Na} \\ \mathrm{O} \\ | \\ \mathrm{C_2H_5O{-}C} \\ \| \\ \mathrm{HC} \\ | \\ \mathrm{COOC_2H_5} \end{array} + \mathrm{RX} = \begin{array}{c} \mathrm{Na} \\ \mathrm{O} \\ | \\ \mathrm{C_2H_5O{-}C{-}X} \\ | \\ \mathrm{HCR} \\ | \\ \mathrm{COOC_2H_5} \end{array} = \mathrm{NaX} + \begin{array}{c} \mathrm{COOC_2H_5} \\ | \\ \mathrm{HCR} \\ | \\ \mathrm{COOC_2H_5} \end{array}$$

(I)

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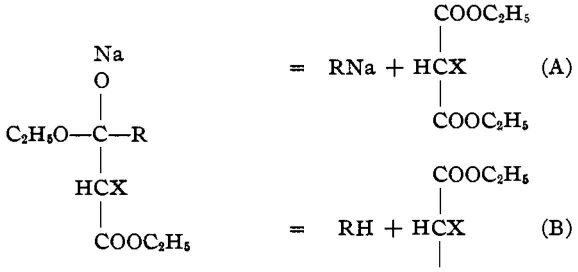
[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy by Frank Clifford Whitmore.

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

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

(X), and the addition compound would have Formula I, which then would easily lose sodium halide forming the substituted malonic ester. There are exceptional cases, however, in which the organic radical (R) is more negative than the halogen (X), especially if this is bromine, or, better still, iodine, then the addition compound will have Formula II and can break up in two different ways. If the radical can combine with sodium, this salt will be easily formed with halogen malonic ester as the secondary product (A). If it cannot combine with sodium, the addition compound should be much more stable than in the two preceding cases, but on acidification the hydrogen compound of the radical will be formed, leaving halogen malonic ester (B).



(II)

$$\begin{array}{c} \text{Na} \\ \text{O} \\ | \\ C_2H_5O\text{—}C\text{—}R \\ | \\ HCX \\ | \\ COOC_2H_5 \end{array} \quad \begin{array}{l} = RNa + \begin{array}{c} COOC_2H_5 \\ | \\ HCX \\ | \\ COOC_2H_5 \end{array} \qquad (A) \\ \\ = RH + \begin{array}{c} COOC_2H_5 \\ | \\ HCX \\ | \\ COOC_2H_5 \end{array} \qquad (B) \end{array}$$

This theory also applies to other esters, which can form enol sodium salts like acetoacetic ester, or camphocarboxylic ester. It will be more convenient to postpone to a second paper the discussion of the apparently similar reactions, which are obtained with sodium alcoholates. It should be borne in mind that the course of most reactions is influenced by several conditions. All that we claim is that the condition stated in our theory is always important and often controls the course of the action.

The idea that the formation of an addition compound is the first stage of the sodium malonic ester reactions is not new, as it was first published by Michael[1] in 1888, and in a somewhat different form by Nef[2] in 1891. In 1905 Michael[3] tried to isolate one of the addition compounds, but his results have been questioned.[4] The original part of this theory is the idea that the sodium exercises a directing influence on the manner of the addition, but, after this had been published,[5] a more careful study of the literature showed that it also had been anticipated by von Findeisen[6] to explain his results from the action of tolylsulfochloride on sodium acetoacetic ester—results which had already been obtained by Kohler and Mac-

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[1] *J. prakt. Chem.*, **37**, 487 (1888).

[2] *Ann.*, **266**, 59 (1891). Compare also Michael, *J. prakt. Chem.*, **46**, 190 (1892).

[3] *Ber.*, **38**, 3217 (1905).

[4] Paal, *Ber.*, **39**, 1436, 2859 (1906); **41**, 58 (1908); **42**, 277 (1909).

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

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

Donald.[1] Von Findeisen, however, did not attempt to make a more general application of the theory, or to test it by further experiment.

We have found only two different explanations of the reactions of sodium malonic ester, both of which were advanced by Nef. The first[2] explains the usual reactions by supposing that the alkyl halide dissociates into the halogen acid and a methylene compound, to which malonic ester is then added.

$$\begin{aligned}&CH(CONaOC_2H_5)(COOC_2H_5) + RCH_2I = \\ &\qquad RCH + NaI + CH_2(COOC_2H_5)_2 = RH_2CH(COOC_2H_5)_2 + NaI.\end{aligned}$$

It seems to us that a fatal objection to this theory is found in the fact that it does not explain such reactions as the formation of benzoylmalonic ester from benzoylchloride, or the conversion of trichlorotrinitrobenzene into dichlorotrinitrophenylacetic ester[3] (a product of the decomposition of the original malonic ester).

Nef's second theory[4] deals with the less usual reactions, in which hydrogen takes the place of a halogen. Here he assumes an addition of malonic ester to the halogen,

$$C_6H_5C \equiv C - IH(CH(COOR)_2) \longrightarrow C_6H_5C \equiv CH + CHI(COOR)_2,$$

and that the addition compound at once falls into the hydrogen derivative and the substituted malonic ester.

Among the objections to this theory, which have occurred to us, the following seem of especial weight: The work described in this paper shows that the addition compound is not made up of *free* malonic ester and the other reagent, as maintained by Nef, but contains sodium; and while such a product might be expected with iodine because of the analogy between $K - I = I_2$ and Nef's compound, $Na - I = (CH(COOR)_2)R'$ (in which R' is a negative radical), it is much less likely that it would be formed with bromine, for which we can find little analogy; and what we know of chlorine makes it very improbable that such a compound could be derived from it. In fact Nef emphasizes this point to explain the difference in behavior of the bromo and iodophenylacetylenes on one side and the chloro compound on the other. Later, however, Willcox,[5] in a paper from Nef's laboratory, showed that the behavior of the ethylsulfuric chloride made it necessary to extend the theory to the chlorine compounds in the face of this acknowledged objection.

[1] *Am. Chem. J.*, **22**, 228 (1899).

[2] *Ann.*, **298**, 263 (1897).

[3] Jackson and Smith, *Am. Chem. J.*, **32**, 174 (1904).

[4] *Ann.*, 308, 306 (1899). In this paper he says that C. L. Jackson and his scholars have never detected the ethanetetracarboxylic ester as the other product of these reactions. This is a mistake, as its presence was reported in 1890, Jackson and Moore, *Am. Chem. J.*, **12**, 7, and Jackson and Dunlap, *Ibid.*, **18**, 117 (1896), while tartronic acid was detected even earlier, Jackson and Robinson, *Ibid.*, **11**, 541 (1889).

[5] *Am. Chem. J.*, **32**, 449 (1904).

Nef's addition compound contains the halogen already combined with sodium, and his theory assumes that in decomposing the halogen breaks away from the sodium to combine with the carbon of the malonic ester, but certainly such a startling hypothesis cannot be accepted, until it has been supported by most convincing evidence.

According to Nef's theories the formation of substituted malonic esters and the replacement of halogen by hydrogen are brought about in entirely different ways, so, for instance, to explain the formation of bromotrinitrophenylmalonic ester from tribromotrinitrobenzene[1] one of the atoms of bromine must have taken up sodium and the malonic ester residue, and another have been split off as hydrobromic acid, if this were possible, but no reason is given to explain why these two atoms of bromine should react entirely differently. Until these objections are removed, it seems to us that our theory should be preferred to those of Nef, as it explains all these observations in a satisfactory manner, as will be shown in our second paper.

In continuing the study of our theory we have tried to submit it to the test of experiment in two ways: First, by isolating the addition compound predicted by it, with results described in this paper; and, second, by studying the effect on the course of reaction of the relative attraction for sodium of the two radicals added, which will be described in a second paper.

Before discussing our quantitative experiments on the addition compound the proofs of its formation may be given. When the pale yellow bromotriiododinitrobenzene is treated with colorless sodium malonic ester in the cold, the mixture turns dark blood red, and if this solution is acidified, the color is discharged, owing to the formation of bromodiiododinitrobenzene and ethanetetracarboxylic ester (or iodomalonic ester), which are colorless, or nearly so. These changes of color, therefore, can be due only to the formation and destruction of a new compound under the conditions predicted by our theory; and the only compounds we can find, which could be formed under these conditions, are our addition compound, or one of the strongly colored salts of a quinol nitro acid;[2] but the latter substance on acidification would give the original triiodocompound, and certainly could not form the iodomalonic ester and bromodiiododinitrobenzene actually obtained, so this alternative must be rejected, and there is left as the only cause of this red color the formation of the addition compound required by our theory. The similar observations when 1,3,5-triiododinitrobenzene was treated with sodium malonic ester[3] furnishes us with another undoubted case of a colored addition

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[1] Jackson and Moore, *Am. Chem. J.*, **12**, 7 (1890).

[2] Jackson and Gazzolo, *Ibid.*, **23**, 376 (1900).

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

compound; and we may have observed many others, as a marked change of color was observed in every one of the 83 reactions studied in this laboratory, in which a nitrohalogen aromatic compound was treated with sodium malonic ester, sodium acetacetic ester, or a sodium alcoholate, but, although some of these colors may have been caused by one of our addition compounds, we can prove this to be the case only in the two reactions already given, as in each of the others it was possible a quinol nitro salt was formed and frequently also a colored salt of one of the reaction products.

The second proof of the formation of our addition compound is furnished by its solubility, as 10 cc. of absolute alcohol dissolve over 10 g. of the red product, but only 1.5 g. of sodium malonic ester and 0.043 g. of bromotriiododinitrobenzene, so there was in solution more than 6 times the weight of solid, which would have been dissolved, if there had been only a mixture of the two components.

This red compound made from bromotriiododinitrobenzene and sodium malonic ester is particularly well adapted for study, because it is very stable, keeping unaltered for nearly a year, is formed almost quantitatively, and the main reaction is not embarrassed by parallel or subsequent reactions. Most of the other addition compounds we have considered are inferior to this in at least one, or sometimes in all three, of these respects.

After preliminary experiments had established the comparative stability of this compound in the cold, and had shown that it could be obtained from its solutions only by evaporation, we were confronted with the problem of determining the composition of a very soluble amorphous substance, for, although in one experiment we had obtained crystals, which seemed to be the addition compound, in a year and a half of attempts to prepare them again, we never observed the least sign of crystallization. Owing to the difficulty in purifying such a substance, we first made a set of analyses of specimens containing the addition compound mixed with a known quantity of one or the other reagent.

As the bromotriiododinitrobenzene is only slightly soluble in absolute alcohol, preparations were made with a sufficient excess of this reagent to saturate the alcohol used, and leave a small quantity of the solid. After the reaction with sodium malonic ester had taken place, the solution was filtered off, a portion evaporated *in vacuo* (it decomposed, if warmed), and the amount of sodium in the residue determined. The weight of bromotriiododinitrobenzene which dissolved in the volume of alcohol used, was determined by a parallel experiment, and on subtracting this from the weight of the residue there was left the weight of the addition compound containing the sodium. Possible weak points in this method of attack were that the reaction might not run to an end, and that the presence of the addition compound might change the solubility of the substituted benzene. The first of these difficulties evidently did not exist, however, since the percentages of sodium agreed within 0.2% with that calculated for $(C_6BrI_3(NO_2)_2)(CH(CONaOC_2H_5)(COOC_2H_5))$, and the absence of the second was proved by the fact that solutions containing much of the addition compound gave the same analytical results as the more dilute, which would have been impossible, if the size of the correction had been affected by the presence of this substance. Similar experiments were tried with a known excess of sodium malonic ester, the solvent being a mixture of benzene and alcohol, which takes up but little of this substance. Applying the correction in this case for the amount of sodium malonic ester dissolved, the percentage of halogens in the residues differed from that calculated for the addition compound by only 1.25% in the worst case. Here, again, the agreement is better than we expected, as this correction would be seriously affected by the moisture and carbon dioxide of the air forming malonic ester, which would add to the weight of the substance analyzed. Exposure to the air was avoided as completely as possible, and evidently with good success, as the error is little, if at all, greater than would be expected from the larger size of the correction than in the preceding case.

These determinations do not *prove* the existence of the addition compound, as they were made with unpurified residues, which did not crystallize or show any other criterion of their freedom from impurities beside the known excess of one of the reagents, but they certainly furnish a strong argument in favor of its existence, as the first series proves that a given volume of alcohol in presence of sodium malonic ester takes up more bromotriiododinitrobenzene than it can alone, and this additional amount dissolved is just sufficient to form a compound made up of one molecule of each reagent. This amount is considerable, for instance in one determination the alcohol, which would normally have taken up only 0.0622 g., with the sodium malonic ester dissolved 0.2397 g. In the second series the bromotriiododinitrobenzene caused the benzene and alcohol to dissolve an amount of sodium malonic ester in addition to that, which would be taken up by the solvent alone, exactly enough to form this same compound.

We tried next to obtain a pure specimen of the red addition compound, using the constituents in molecular proportions in a mixture of benzene and absolute alcohol. The resulting solution, after it had stood several days, was evaporated *in vacuo* till sufficient solid had deposited, and, after this had been filtered out, a second solid red fraction was obtained from the filtrate, but the filtrate from this yielded a dark red liquid. Analyses showed that the least soluble fraction contained bromotriiododinitrobenzene, the most soluble fraction malonic ester, or its sodium salt, while the intermediate fraction gave a percentage of halogens agreeing with that for the addition compound. These experiments therefore showed that the substance could be purified by this fractional evaporation. It is to be observed that with equal molecules of the two reagents the action does not run to an end, whereas our previous series of experiments indicated that with a large excess of one of the reagents the other was completely used up.

The way had now been cleared for the study of the homogeneity of the addition compound. A large amount of it was made, as in the second series of experiments, and submitted to an elaborate systematic fractionation, in which 29 solid fractions were obtained. This work was tedious in the extreme, as it was necessary to carry on all the evaporations at ordinary temperatures. Analyses of the most and least soluble fractions showed that the unaltered portions of the two reagents accumulated in these as in the second series, and, after these had been rejected, a considerable amount of intermediate material was left, which was divided into 4 fractions according to solubility, when analyses showed that the percentage of halogens in the least soluble fraction agreed absolutely with that in the most soluble. It seems to us that this proves the red addition product is a definite compound with the composition

$$[C_6BrI_3(NO_2)_2][CH(CONaOC_2H_5)(COOC_2H_5)].$$

We also describe in this paper some improvements in the preparation of triiodoaniline, which make it possible to obtain this substance in a state of purity with tolerable certainty.

Experimental.

Preparation of Triiodoaniline (Monochloride of Iodine).—Success in this preparation depends in great measure on the purity of the monochloride of iodine used, since a slight excess of free iodine, or, worse still, of trichloride of iodine, gives a black product, which produces distressing results, when submitted to the diazo reaction. Our predecessors tried to avoid this difficulty by continuing the action of the chlorine on the iodine until a few yellow crystals of the trichloride appeared, when the attempt was made to remove this impurity either by heat or the addition of iodine.[1] These methods proved unsatisfactory, partly because the amount of impurity was considerable, since much of the trichloride was needed to saturate the monochloride, before the crystals appeared, and partly because the action of heat in removing it was incomplete without too great a loss of the monochloride, or the action of iodine on the trichloride was exceedingly sluggish. We have accordingly substituted for them a process, in which the monochloride is prepared with little more than a trace of free iodine, and the temperature, at which it is driven over into the aniline hydrochloride, is kept so low that most of this iodine is left

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[1] *Am. Chem. J.*, 26, 55 (1901); 46, 557 (1911).

behind. Our process is based on Stortenbeker's[1] work on the equilibria in the system iodine–chlorine. Out of 12 preparations we obtained with it white, or nearly white, triiodoaniline in 11, the twelfth being only pale brown, whereas a white product was the exception rather than the rule with the older processes.

A rapid stream of chlorine, dried by several spiral washing tubes of strong sulfuric acid, was passed over 42 g. of cold iodine (the amount for 10 g. of aniline) in a flask. The point at which the process should be stopped was determined by watching carefully the appearance of the product after all the crystals of iodine had disappeared. If some of the liquid was shaken up on the side of the flask at this point, it left a sticky opaque coating, but, as more chlorine was added with constant shaking, the liquid flowed from the side of the flask without wetting it; which in turn was followed by a more perfect liquefaction, so that the side of the flask was wet once more, leaving a slightly streaked layer red and transparent, when held to an electric light. The action of the chlorine was stopped when this streakiness had almost, but not quite, disappeared. It seemed to be caused by free iodine, which in this way was reduced to a minimum with no danger of forming any of the much more injurious trichloride of iodine. If the action of the chlorine was carried too far, the red transparent film on the side of the flask was entirely uniform. Such a preparation solidified on cooling to a mass of long, dark red needles, but gave an impure triiodoaniline as the rapid crystallization was brought about by a little trichloride of iodine. A specimen prepared by stopping the chlorine at the right point did not solidify even after standing for several days at 0°, probably because the slight excess of iodine prevented the crystallization. This was left behind in the flask, after the monochloride had been drawn over into the solution of aniline hydrochloride.

To prepare the triiodoaniline 10 g. of freshly distilled aniline were dissolved in 1 liter of strong hydrochloric acid, twice the quantity used by our predecessors, which, although it slightly lowered the yield, gave a purer product. The solution was then diluted to 7–8 liters and a rapid stream of air sucked through it, which had previously passed through the weighed flask containing the monochloride of iodine heated to 20–30° in a water bath. This very low temperature reduced any decomposition of the monochloride to a minimum, and also kept back most of the free iodine. After the calculated amount of the monochloride had volatilized, the solution with the flocculent precipitate was allowed to stand over night, filtered through a large cloth bag, as suction rendered the precipitate unmanageable, washed free from hydrochloric acid, and dried on a steam radiator. The yield of crude triiodoaniline amounted in 11 experiments to 480 g. from 568 g. of the monochloride of iodine, that is 85% of the

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[1] *Z. physik. Chem.*, 3, 11.

theory. The products varied from light gray melting 165–172° (uncorr.) to pure white melting as high as 178° (uncorr.). Pure triiodoaniline melts at 185.5°. If the monochloride of iodine was a bad preparation, or the triiodoaniline was black, it saved time to throw it away, rather than to try to get a pure substance from it.

The crude triiodoaniline was extracted several times with small quantities of boiling alcohol, which left a residue of the pure substance melting at 185° (uncorr.) instead of 185.5°. The first of these alcoholic extracts were very dark, even when the crude triiodoaniline was nearly white. From them two substances were obtained. The first by cooling the mother liquors from a specially impure triiodoaniline, after they had been evaporated to small volume. The substance thus obtained proved after several recrystallizations from alcohol to have the constant melting point 95° (uncorr.), and is therefore diiodoaniline, which melts according to Rudolph and Michael and Norton[1] at 95–96°. This inference was confirmed by the analysis of a slightly impure specimen.

Diiodoaniline Hydrochloride.—The second compound was obtained in quantity from a specimen of the triiodoaniline, which had been dried without washing it free from hydrochloric acid, but small amounts of this and the free diiodoaniline were formed in every preparation of triiodoaniline. The alcoholic extract from the specimen first mentioned deposited it in silvery white plates melting near 200°. As it was found impossible to purify it by crystallization, which, on the contrary, rendered it more impure, the original crystals were dried *in vacuo* and analyzed I. Another sample was made by dissolving diiodoaniline in dry benzene and treating it with dry hydrochloric acid gas. The white precipitate was dried *in vacuo*. II.

I, Subst. 0.1854, II, 0.2286, 2090; AgCl + AgI, 0.2973, 0.3676, 0.3379. Calculated for $C_6H_3I_2NH_2HCl$: Cl + I, 75.88; found: 75.73, 75.95, 76.37.

The two preparations showed the same properties. Silver white plates blackening slightly at 185° and melting with decomposition at 207° (uncorr.). Water does not act on it in the cold but when hot decomposes it into diiodoaniline and hydrochloric acid, as would be expected from the fact that the triiodoaniline hydrochloride has not been prepared.

Preparation of Bromotriiododinitrobenzene.—Ten grams of the triiodoaniline prepared and purified as described above were mixed in a heavy walled Erlenmeyer flask with 120 cc. of glacial acetic acid and 50 cc. of fuming hydrobromic acid, and 3 g. of powdered sodium nitrite added so slowly that an entire day was occupied by the addition, the flasks being kept stoppered during the reaction, which seemed to succeed better under this slight pressure. After standing over night the diazo compound was decomposed by warming, and the solid product extracted

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[1] *Ber.*, 11, 78, 109 (1878).

with small quantities of alcohol, till the residue melted at 142° (instead of 146°). It was found not worth while to use the crystals obtained from the extracts. This process differs in several particulars from that given by Bigelow and one of us,[1] the most important being the use of fuming hydrobromic acid instead of the constant boiling acid. This was obtained by passing hydrobromic acid gas into a constant boiling specimen made from sulfuretted hydrogen, bromine and water. The bromotriiodobenzene was sometimes gray instead of yellow, but gave the dinitro compound without difficulty.

The bromotriiodobenzene melting not below 142° was boiled for 4 hours with nitric acid of sp. gr. 1.51 in a flask fitted to a return condenser by a ground joint, and instead of allowing the mixture to cool the hot acid was decanted from the crystals, which were then washed by decantation with water. These white, feathery crystals always melted above 280° and sometimes at 290° (instead of 292°). The yield was nearly 50%. The hot acid contained only material so impure and in such small amount that it was not worth while to purify it. The improvements introduced by us into these preparations remove the necessity of the tedious crystallizations, which were a feature of the earlier work.

The Addition Product of Bromotriiododinitrobenzene and Sodium Malonic Ester.—When these two substances are mixed in absolute alcohol, or benzene solution, a dark blood-red color appears, which is destroyed by acidification with the formation of bromodiiododinitrobenzene and ethanetetracarboxylic ester as the principal products. The red substance formed in this way shows considerable stability if protected from water and acids. A specimen of the solution made with equal molecules of the components did not lose its color, or form any precipitate even after standing over two years in a sealed tube. In order to test its stability under more exacting conditions we made a preparation in benzene and alcohol with 4 molecules of the ester to one of the benzene compound, as we thought at that time this excess would favor the decomposition of the addition compound, but after standing 3 weeks no test for a sodium halide was obtained in the white precipitate, which had come down, and this was therefore only sodium malonic ester precipitated slowly by the benzene. To meet the objection that sodium iodide might have been formed but retained in colloid solution in the benzene,[2] the experiment was repeated with exactly the same result in absolute alcohol, where there is little chance of the formation of a colloidal solution. A fuller study led us to believe that varying the proportion of sodium malonic ester from 1 to 5 molecules had no effect upon the reaction, except that an excess made the red color appear sooner in benzene and alcohol, and the bromotriiododinitro-

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

[2] Compare Paal and Kuhn, *Ber.*, **39**, 2859 (1906).

benzene dissolve more rapidly in alcohol, than when the reagents were used in equivalent amounts. Although the red solution was so stable in the cold, it decomposed, when heated for 2 hours, forming a considerable precipitate of sodium iodide whether in alcohol or in alcohol and benzene. It was necessary, therefore, to carry on all the evaporations in our experiments at ordinary temperatures, which greatly increased the tediousness of the work.

In our attempts to isolate the red addition compound we tried first to precipitate it from its benzene solution by the addition of other solvents, but without success, for although ligroin precipitated a red oil, this seemed less manageable than the residues left after evaporating off the benzene; and no other solvent produced any effect, if it was dry and free from acid. As it is a sodium salt we next tried to replace the sodium by some other metal in the hope of getting an insoluble product. For this purpose the red alcoholic solution was treated with silver nitrate, calcium chloride, ferric chloride, or mercuric chloride dissolved in absolute alcohol, but in no case was a precipitate formed.

The negative results of these experiments reduced as to obtaining the substance by evaporation, which was carried on to best advantage in a Hempel *vacuum* desiccator charged with fused potassium hydroxide. With this 175 cc. of a mixed benzene and alcohol solution were reduced to 15 cc. in about 20 hrs. instead of taking 3 days or more, as was the case when a common *vacuum* desiccator with sulfuric acid was used. We tried also passing a stream of air through the liquid from a capillary tube, while a *vacuum* was maintained, as in distillation under diminished pressure, but this worked no more rapidly than the Hempel desiccator, and was more apt to lead to decomposition because of the difficulty in removing all traces of moisture and carbon dioxide from so large a volume of air. The residues at first were red oils, or tars, which, after all the solvent had gone, were converted into amorphous viscous solids of a dark red color. If the process had succeeded, these showed no signs of crystallization; if it had not, white crystals were deposited in small amount, which were either unaltered bromotriiododinitrobenzene, or ethanetetracarboxylic ester formed by carbon dioxide from the air. Such specimens were rejected. The result was the same, whether the reaction took place in benzene and alcohol, or in absolute alcohol alone.

After working on this substance for half a year one preparation containing a large excess of malonic ester deposited a few minute clusters of crystals, which looked black to the naked eye, but under the microscope appeared as red plates. As they looked not unlike iodine, they were carefully tested for this substance with negative results. They dissolved easily in alcohol with a red color, and kept between two sealed watch glasses apparently unaltered for nearly a year, after which they became tarry. The quantity was too small for decisive study, but the appearance and properties justify the surmise that they were crystals of the addition compound. For a year and a half we tried by every modification of the process we could devise to get such crystals again, but have not even caught a glimpse of them. Substituting malonic methyl ester for the ethyl compound gave no better result in spite of the greater tendency of methyl compounds to crystallize.

Sodium Determinations Made with the Impure Addition Compound.—As at first there seemed little chance of obtaining a pure specimen of the addition compound, we determined the amount of sodium in a preparation containing a known amount of the bromotriiododinitrobenzene. The results were even better than we had hoped.

The specimens were prepared in absolute alcohol, in which the red product is very soluble, whereas a series of determinations showed that 100 cc. of absolute alcohol dissolve of the bromotriiododinitrobenzene only 0.416 g. at 15°, 0.420 g. at 16°, 0.432 g. at 20°, and 0.440 g. at 21°. We proceeded as follows:

The clean sodium was weighed to milligrams in a weighing bottle under kerosene oil, and after drying quickly with filter paper was dropped into absolute alcohol, which, like all used in this work, had been distilled after treatment with a little sodium to remove the last trace of water. The malonic ester corresponding to the sodium was then weighed to centigrams, and also an amount of bromotriiododinitrobenzene, which gave one molecule of this substance for each molecule of the ester, and an excess more than enough to form a saturated solution with the amount of absolute alcohol used. The substituted benzene was first boiled with absolute alcohol, which dissolved only a small part of it, and after it had been cooled, the malonic ester was added, and finally the cool sodium ethylate solution. A dark red color appeared instantly, and after 5 minutes most of the solid had gone into solution. The flask was allowed to stand at about 20° for 2 or 3 days with occasional shaking to complete the reaction. Another flask was prepared with portions of the same specimens of bromotriiododinitrobenzene and absolute alcohol, and exposed to exactly the same conditions to determine the amount dissolved. At first very dilute solutions of the red compound were used, so that its presence might not change the solubility of the bromotriiododinitrobenzene. Later, stronger solutions were used, in which the correction for the dissolved bromine compound was much smaller in proportion to the amount of red product. As the two sets of corrected results agree with each other, the method of correcting for the presence of the dissolved benzene compound must be at least approximately accurate.

After the two flasks had stood for at least 3 days, the temperatures were taken, the contents filtered to remove undissolved bromotriiododinitrobenzene, and the filtrates kept in well-stoppered bottles, which as a further precaution were sealed with hard paraffin. 25 cc. of the filtrate were transferred to a platinum crucible and the solvent evaporated in a vacuum desiccator over sulfuric acid and a trace of potassium dichromate, as experiment had shown that evaporation on the steam bath decomposed the red substance. After most of the solvent had evaporated, a fresh portion of 25 cc. of the filtrate was added, and the process continued until a sufficient amount of residue had been obtained. The residue was brought to constant weight *in vacuo*—a very tedious process, as the viscous solid retained traces of the solvent obstinately. It was found later that the work would have gone less slowly with a potassium hydroxide

Hempel desiccator; as it was, the shortest of these determinations lasted 10 days. The weighed product was then treated with a little strong nitric acid and strong sulfuric acid in the cold. This must be done with great caution to avoid spattering, as the decomposition was attended with a vigorous effervescence. The sodium was then determined in the ordinary way. Before calculating the analyses the weight of substance was corrected by subtracting from it the weight of bromotriiododinitrobenzene contained in the same volume of the solvent, which had been submitted to the same conditions in the blank experiment.

Residue, 0.3725, 1.6648, 2.4136. Correction, 0.0622, 0.4662, 0.5080. Subst., 0.3103, 1.1986, 1.9056; Na_2SO_4, 0.0284, 0.1016, 0.1653. Calculated for $C_6BrI_3(NO_2)_2CHCONaOC_2H_5COOC_2H_5$: Na, 2.85; found: 2.96, 2.75, 2.81.

The results agree with each other and with the theory better than we had expected.

Determinations of Halogens in the Impure Addition Compound.—In these analyses the quantity of sodium malonic ester used was so large that some of it remained undissolved in the solvent consisting of 1 part absolute alcohol to 12 of benzene (dried with sodium). The correction to be applied for the dissolved sodium malonic ester was determined by a parallel blank experiment in each case. In all other respects the procedure was the same as in the determinations of sodium. The halogen determinations were made by the method of Carius in a portion of the residue dried *in vacuo* to constant weight.

Residue, 0.3148, 0.3398, 0.3279. Correction, 0.1205, 0.1300, 0.1255. Subst., 0.1943, 0.2098, 0.2024; AgI + AgBr, 0.2191, 0.2368, 0.2248. Calc. for $C_6BrI_3(NO_2)_2CHCONaOC_2H_5COOC_2H_5$: I + Br, 57.08; found: 58.20, 58.34, 57.34.

The agreement here, although not so good as with the sodium, is as close as could be expected, when it is remembered that the correction may be seriously interfered with by the moisture and carbon dioxide of the air converting sodium malonic ester into the soluble free ester.

Fractionation of the Addition Compound.—To determine whether the red product was a compound or a mixture, and to obtain it, if possible, free from impurities, specimens of it were next divided into fractions according to solubility. Our first experiments aimed at preparing only 3 fractions. 3.86 g. of malonic ester and 15.1 g. of bromotriiododinitrobenzene (these are not far from molecular proportions) with 0.55 g. of sodium were allowed to react in a mixture of alcohol and benzene for at least 3 days, after which 175 cc. of the solution were evaporated in a Hempel *vacuum* desiccator charged with potassium hydroxide until its volume had been reduced to 10 cc. At this point sufficient solid had been deposited to render the liquid thick, and it was filtered. To secure the filtration of this viscous mass without decomposition by the carbon dioxide, or water in the air, the last part of the evaporation was carried on in a small Erlenmeyer flask, the neck of which fitted the platinum Gooch crucible to be used for the filtration. The hardened filter paper was carefully fitted to the crucible, and the filtrate was received in a small test tube within the suction flask, which should not be too large. When the substance was ready for filtration, the Erlenmeyer flask was removed from the desiccator, stoppered, and fitted with a thin rubber hose on its neck; the stopper was then replaced by the inverted Gooch crucible with its suction flask, the adjustments being made as rapidly as possible. The suction was started, the apparatus inverted, and the filtration begun. It was found that even a good water pump did not give pressure enough to filter this viscous mass, so a powerful cylinder pump was used, but even with this the filtration lasted several hours. Fortunately, the dark red amorphous solid was not viscous enough to clog the filter. If the process had succeeded, the solid was completely soluble in a very small quantity of absolute alcohol. In some cases, however, it left a slight white residue of bromotriiododinitrobenzene. Specimens of these least soluble fractions from different preparations are numbered I and II in the analyses.

During the filtration the low pressure caused the evaporation of part of the filtrate, so that a second filtration gave a solid like the first, except that it showed a somewhat deeper red color. Specimens of such intermediate fractions are numbered III, IV, V in the analyses. When we tried to secure a third fraction in this way, very little solid was deposited, but we obtained a deep red liquid, which showed no sign of solidification on standing *in vacuo*, or by cooling with a freezing mixture. It was odorless, and mixed easily with benzene or alcohol. Analyses of such most soluble fractions are numbered VI and VII.

	I.	II.	III.	IV.	V.	VI.	VII.
Subs	0.2545	0.2451	0.2273	0.3203	0.2465	0.3070	0.3589
AgI + AgBrO	0.2915	0.2797	0.2522	0.3569	0.2770	0.3225	0.3744
Found, I + Br	59.12	58.89	57.27	57.51	58.01	54.24	53.86

Calc. for $C_6BrI_3(NO_2)_2CHCONaOC_2H_5COOC_2H_5$: I + Br, 57.08.

A similar experiment with sodium malonic methyl ester gave a least soluble (VIII) and an intermediate fraction (IX).

VIII. Subst., 0.2265, IX, 0.2532 AgI + AgBr, 0.2735, 0.2908. Calc. for $C_6BeI_3(NO_2)_2CHCONaOCH_3COOCH_3$: I + Br, 59.19; found: VIII, 62.33; IX, 59.30.

The intermediate fractions, III, IV, V, and IX, agree sufficiently well with the percentage required by the formula. The less soluble fractions, I, II, VIII, seem to contain a slight impurity of bromotriiododinitrobenzene; the more soluble, VI and VII, one of sodium malonic ester.

A more elaborate fractionation on a larger scale was next undertaken with the object of breaking up the intermediate portion into smaller fractions, the analyses of which would settle the question, whether it was a homogeneous compound, and also, when this work was started, we had not given up the hope of obtaining the red compound in crystals.

A large amount of the red substance was made from equal molecules of the two reagents in a mixture of alcohol and benzene, and after standing 25 days, during which time no solid separated, was evaporated in a Hempel desiccator over potassium hydroxide, and fractionated systematically from absolute alcohol. 29 different fractions were separated—no light task even with the quicker evaporation in the Hempel desiccator, and in this way a large amount of material of intermediate solubility was obtained, which, judging from the results of the previous experiments, should consist of the pure addition compound. This presumably pure material was then divided into 4 fractions, X, XI, XII and XIII, of which the least soluble was X, the most soluble XIII. To show that the impurities had been removed in the preparation of the material for X to XIII, analyses are added of the most impure fractions rejected in making it, the least soluble being XIV, the most soluble XV. XIV and similar very impure least soluble fractions were pale red, and, when treated with absolute alcohol, left a white residue of unchanged bromotriiododinitrobenzene. All the other fractions were dark red and completely soluble in alcohol.

	X.	XI.	XII.	XIII.	XIV.	XV.
Subst.	0.2236	0.2584	0.4532	0.3087	0.3108	0.2322
AgI + AgBr	0.2461	0.2838	0.4968	0.3398	0.3600	0.2407
Found: I + Br	56.80	56.69	56.58	56.80	59.78	53.43

Calc. for $C_6BrI_3(NO_2)_2CHCONaOC_2H_5COOC_2H_5$: I + Br, 57.08.

It seems to us that the inference to be drawn from the agreement between the analysis of the least soluble fraction X and the most soluble XIII is that the material, from which they were obtained, was a definite compound in a state of purity.

Properties of the Addition Compound, $C_6BrI_3(NO_2)_2CH(CONaOC_2H_5)(COOC_2H_5)$.—It is usually obtained as a very dark red amorphous solid, but on one occasion we think it appeared in clusters of needles so dark red as to look black. The solid can be kept as much as a year, if protected from the air, and its solution showed no sign of alteration after standing in a sealed tube for nearly 2 years. Water or an acid decomposes it, the product, in the latter case, being bromodiiododinitrobenzene and iodomalonic ester (or if there is an excess of sodium malonic ester, ethanetetracarboxylic ester). Heat also decomposes the solution, forming a precipitate of sodium iodide. It is very soluble with a blood-red color in all the common organic solvents except ligroin, which precipitates a red oil from its solution in benzene and alcohol. 10 cc. of absolute alcohol dissolve more than 10 g. of the addition compound, and it seems to be equally soluble in benzene. To give an idea of its remarkable solubility we may say that 15 cc. of a mixture of absolute alcohol with some benzene held in solution 19.5 g. of it, and even when cooled to —20° deposited no solid except a little benzene. On evaporating further the red solid appeared before the volume had been reduced to 10 cc. No salts containing other metals could be obtained from the addition compound.

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[CONTRIBUTION FROM THE LABORATORY OF THE DODGE & OLCOTT CO.]

AZULENE, A BLUE HYDROCARBON. II.

BY ALFRED E. SHERNDAL.

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Since the publication of the preliminary notice of the isolation of the remarkable new hydrocarbon which occurs in so many of the essential oils,[1] the following further work has been carried out, and is described below:

(1) The preparation of a picrate, and its analysis.

(2) The preparation of artificial blue oils from various oils of the sesquiterpene type.

(3) The isolation and identification, by means of the picrate, of azulene from the blue sections of the oils of cubebs, camphor, and from the artificial blue gurjun oil.

(4) The complete reduction of azulene to a colorless dihydrosesquiterpene.

The picrate is readily formed by combining the alcoholic solutions of its constituents, and crystallizes out almost immediately in the form of jet black, shiny needles, melting without decomposition at about 120°, and containing one mol of picric acid to one mol of azulene. This ready formation of a picrate is strong evidence that the hydrocarbon possesses an aromatic structure, since only this class of hydrocarbons has been found to yield additive compounds with picric acid, etc.[2] No true picrates of the hydroaromatic hydrocarbons have been prepared, the so-called picrates of pinene and thymene,[3] being in reality picric acid esters, from which the original hydrocarbons cannot be regenerated. They also differ from the picrates of the aromatic hydrocarbons in conditions of formation, stability, etc. The picrate of azulene, on the other hand, resembles the true additive compounds of picric acid with the aromatic hydrocarbons in ease of formation, decomposition by water or dilute alkalies with regeneration of the original hydrocarbon, melting point, etc. It provides an excellent means of establishing the identity of the blue substances isolated from various oils, and of effecting a final and complete purification of the blue hydrocarbon.

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[1] THIS JOURNAL, **37**, 167 (1915).

[2] Bruni, *Chem. Ztg.*, **30**, 569 (1906); Küster, *Ber.*, **27**, 1101 (1894).

[3] Lextreit, *Compt. rend.*, **102**, 555 (1886); Semmler, "*Die aetherischen Öle*," II, 253.