CXXXVII.—*The Formation and Properties of Dithio-
ketones ($R_2C:S:S$) and Dithio-ethers ($R_2S:S$).
Part II.*

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THE experiments described in this paper afford clear evidence that the interaction of sulphur monochloride with compounds containing the methylene radicle depends on the nature of the groups attached to the two remaining valencies of the carbon atom. Thus, if these valencies carry neutral groups such as $CO\cdot NH_2$, for example, in malonamide, $CH_2(CO\cdot NH_2)_2$, no reaction occurs. If, however, one of these carboxyamido-groups is replaced by the carbethoxy-group, as in ethyl malonamate, $CH_2(CO_2Et)\cdot CO\cdot NH_2$, or if the neutral character of either or both of the carboxyamido-groups is disturbed by the substitution of a phenyl, tolyl, or similar group at the nitrogen atom, as in the compounds $CH_2(CO\cdot NH_2)\cdot CO\cdot NHPh$, $CH_2(CO\cdot NH\cdot C_{10}H_7)_2$, $CH_2(CO\cdot NH\cdot C_7H_7)_2$, interaction with sulphur monochloride readily occurs with the formation of dithioketones of the type $S:S:C(CO\cdot NH_2)\cdot CO\cdot NHPh$.

Moreover, although no definite measurements have as yet been

made, it is evident that the speed of the reaction depends on the electronegative character of the attached groups. For example, sulphur monochloride reacts more vigorously with malondi-phenylamide, $\text{CH}_2(\text{CO}\cdot\text{NHPh})_2$, than with malonomonotolylamide, $\text{CH}_2(\text{CO}\cdot\text{NH}_2)\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_7\text{H}_7$, and the reaction with ethyl malonomotolylamate, $\text{CH}_2(\text{CO}_2\text{Et})\cdot\text{CO}\cdot\text{NH}\cdot\text{C}_7\text{H}_7$, is still more vigorous than with either of the former compounds. In fact, reactions of the last-named type take place at the ordinary temperature with copious evolution of hydrogen chloride.

Wolff and Ott (*Ber.*, 1903, **36**, 3721) have studied the interaction of methyl and ethyl malonates with sulphur monochloride in the presence of anhydrous aluminium chloride and obtained different compounds with the two esters. Since it is well known that sulphur monochloride reacts in different ways under different conditions (Böeseken, *Rec. trav. chim.*, 1905, **24**, 209; Cohen and Skirrow, *T.*, 1899, **75**, 887; P., 1899, **15**, 183; Claus and Krall, *Ber.*, 1871, **4**, 99; Edeleano, *Bull. Soc. chim.*, 1891, [iii], **5**, 173; Roorda Smit, *Ber.*, 1875, **8**, 1445), it was decided to study its reaction with (1) malonic and cyanoacetic esters and (2) their sodium compounds. It is remarkable that the products of these condensations are, in the case of the malonic ester, ethyl ethylenetetracarboxylate, and in the case of the cyanoacetic ester, ethyl dicyanosuccinate, whilst for the sodium compounds they are ethyl ethanetetracarboxylate in the case of the malonic ester, and ethyl dicyanosuccinate in the case of the cyanoacetic ester. A separation of sulphur occurs in every case :

and

where $\text{X}=\text{H}$ or Na .

It has been mentioned in Part I of this series (this vol., p. 382) that dithiomesoxanilide, when nitrated with fuming nitric acid, yields a tetranitro-derivative :

The reaction has now been extended to other dithioketones, for example, to dithiomesoxo- α -naphthylamide, which in the first place gives a tetranitro-derivative :

When, however, nitration is carried further, the dithio-grouping

is broken down and a sulphoxide results, two more nitro-groups entering the naphthalene nuclei at the same time :

Dithiomesoxo- β -naphthylamide and *o*- and *p*-toluidides behave in the same way.

An example of the nitration of a disulphide is furnished by methylmalono-*p*-toluidide disulphide, which, on very careful nitration, yields a dodecanitro-compound :

Clearly, therefore, it is possible to nitrate these compounds without destroying the dithio-grouping, which behaves as a remarkably stable residue. This is obviously a powerful argument in support of the view previously suggested that the dithio-grouping in these compounds is structurally different from that present in $\beta\beta'$ -dichlorodiethyl disulphide and similar compounds and that sulphur monochloride is capable of reacting in two forms,

the first of which gives rise to very stable dithio-compounds (compare Part I of this series) containing the groups

Experiments have been carried out with the object of testing the reactivity of sulphur monochloride towards compounds containing the group $-\text{CO}\cdot\text{CH}_2\cdot\text{CO}-$, when the latter forms a part of a closed ring, and as a large amount of work is being done in this laboratory on the formation and stability of *spiro*-compounds, it was decided to employ typical *spiro*-compounds containing a *cyclohexane* ring. Three such compounds (III), (IV), and (V) (compare Norris and Thorpe, this vol., p. 1190) were selected :

The course pursued in these reactions affords a remarkable example of the difference in the behaviour of similarly constituted substances containing the $-\text{CO}\cdot\text{CH}_2\cdot\text{CO}-$ group towards sulphur monochloride. For, whilst in the compound (III) only one methylene group, namely, that situated between the carbonyl groups, is attacked, with the formation of the dithioketone (VI), in the compound (IV) the reaction proceeds further and involves one of the remaining methylene groups of the dihydroresorcinol ring, the substance (VII) being formed, and in the case of the *spiro*-compound (V), it proceeds yet further, all three of the methylene groups being attacked. The product in this case is the compound (VIII).

In order to obtain further knowledge of the influence on the reaction of sulphur monochloride with methylene groups of neighbouring electronegative residues, experiments with substituted amides containing the group $-\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}-$ were made. The compounds employed were (1) the dianilide, (2) the di-*o*-toluidide, (3) the di-*p*-toluidide, of acetonedicarboxylic acid, and (4) ethyl γ -phenylcarbamyloacetate.

Of these compounds, only (1) and (4) have been described (Besethorn and Garben, *Ber.*, 1900, **33**, 3443), whereas (2) and (3) do not appear to have been prepared. When these four compounds were treated with sulphur monochloride in dry benzene, reaction took place readily, but it was most vigorous in the case of compound (4), the product containing four atoms of sulphur. In cases (1), (2), and (3), although more than two molecules of sulphur monochloride were taken for every molecule of the substituted amide to give ample opportunity for the substitution of dithio-groups for all the hydrogen atoms in the two reactive methylene groups, reaction did not proceed to this extent and the product contained only two atoms of sulphur, one hydrogen atom of each methylene group having been substituted.

This is in accord with what follows from the hypothesis herein suggested, that the reactivity of the two hydrogen atoms of the methylene group is dependent on the total negativity of the two carbonyl groups with their attached radicles. It will be seen in the case of the foregoing substituted amides that the negative effect of the central carbonyl group is divided between the two adjacent methylene groups, so that the total negative effect on each methylene group is smaller than that on a single methylene group when linked as $-\text{CO} \cdot \text{CH}_2 \cdot \text{CO}-$, as in the case of the compounds described in Part I. Hence it is to be expected that the two methylene groups in compounds (1), (2), and (3) will be less reactive than the methylene group in compounds such as malonanilide. However, as soon as the total negativity of the compound is increased by replacing one of the $\text{CO} \cdot \text{NHR}$ groups by a carbethoxy-group, the reactivity is correspondingly increased, and a dithio-compound is produced, analogous to those described above.

The investigation of the exact conditions under which the stability of the dithio-group can be controlled will be the subject of future work.

EXPERIMENTAL.

Dithiomesoxo-p-toluidide.

Malono-*p*-toluidide was prepared by the method of Whiteley (T., 1903, **83**, 24) with the modification introduced by Reissert and Moré (*Ber.*, 1906, **39**, 3300). The best temperature for the condensation is, in this instance, 140° , rising to 160° . The amide (10 grams), sulphur monochloride (5 grams) and benzene (100 grams) were heated together for three hours, and the solid condensation product was then washed with dry benzene and purified by precipitation from its solution in acetone by means of water until it melted at $215-216^\circ$ (Found: S=18.26. $\text{C}_{17}\text{H}_{16}\text{O}_2\text{N}_2\text{S}_2$ requires S=18.60 per cent.).

The *tetranitro*-derivative was prepared by dissolving the thio-compound in sufficient nitric acid (D 1.5) and warming. The nitration product which separated on cooling was collected, washed

with concentrated nitric acid and with water, and dried, when it was obtained as white crystals which melted and decomposed at 255° and assumed a yellow colour on keeping (Found : $N=15.81$; $S=11.82$. $C_{17}H_{12}O_{10}N_6S_2$ requires $N=16.03$; $S=12.21$ per cent.).

Dithiomesoxo-o-toluidide.

Malono-*o*-toluidide was prepared and condensed with sulphur monochloride similarly to the *para*-compound. The product obtained by evaporating the solvent (benzene) was crystallised from a mixture of benzene and light petroleum. It separated in fibrous needles melting at $189-190^{\circ}$ (Found : $S=18.89$. $C_{17}H_{16}O_2N_2S_2$ requires $S=18.60$ per cent.).

The *tetranitro*-derivative was prepared in the same way as the *p*-isomeride and obtained as a yellowish-white powder when the solution in nitric acid was allowed to cool slowly. It melted and decomposed at 165° (Found : $N=16.15$; $S=12.32$. $C_{17}H_{12}O_{10}N_6S_2$ requires $N=16.03$; $S=12.21$ per cent.).

Dithiomesoxo- α -naphthylamide.

Malonodi- α -naphthylamide (6.5 grams), prepared like the toluidide except that the final temperature was 170° , sulphur monochloride (2.5 grams) and benzene (50 c.c.) were heated together and the product was purified by crystallisation from benzene. It formed pale red needles which sintered at 160° and melted with decomposition at 210° (Found : $S=15.70$. $C_{23}H_{16}O_2N_2S_2$ requires $S=15.38$ per cent.).

Tetranitro-derivative.—The dithio-amide (5 grams) was treated gradually with 40 c.c. of nitric acid (D 1.5). After the first violence of the reaction had abated, the mixture was warmed to complete it and then allowed to cool, when the tetranitro-compound separated as an orange-red powder. After being washed with concentrated nitric acid and with water, it melted at 190° with decomposition (Found : $N=14.43$; $S=10.40$. $C_{23}H_{12}O_{10}N_6S_2$ requires $N=14.09$; $S=10.75$ per cent.).

Hexanitro-sulphoxide (Formula I).—This was recovered from the nitric acid washings by dilution with water as a yellow, crystalline substance which decomposed at 135° (Found : $N=16.81$; $S=4.57$. $C_{23}H_{10}O_{15}N_8S$ requires $N=16.71$; $S=4.77$ per cent.).

Dithiomesoxo- β -naphthylamide.

Malonodi- β -naphthylamide was prepared similarly to the α -compound and condensed in the same way. The product was purified

by repeated precipitation by water from its solution in acetone until it melted at 204° with decomposition (Found: $S=15.56$. $C_{23}H_{16}O_2N_2S_2$ requires $S=15.38$ per cent.).

The *tetranitro*-derivative, when prepared and purified as in the case of the α -naphthylamine derivative, was obtained as a pale yellow powder decomposing at 195° (Found: $N=14.04$; $S=10.54$. $C_{23}H_{12}O_{10}N_6S_2$ requires $N=14.10$; $S=10.73$ per cent.).

Dithiomesoxomono-p-toluidide.

Malonomono-*p*-toluidide, prepared by Whiteley's method (*loc. cit.* Compare also Backes, West, and Whiteley, this vol., p. 372), the temperature of the condensation with *p*-toluidine being $120-125^{\circ}$, was condensed (7 grams) with sulphur monochloride (5 grams) in benzene (50 grams) in the usual manner. The product separated from alcohol, on addition of water, in short needles which melted to an oil clarifying at 150° and decomposing at 165° (Found: $S=24.78$. $C_{10}H_{10}O_2N_2S_2$ requires $S=25.20$ per cent.).

Dithiomesoxomonophenylamide.

Malonomonophenylamide, prepared like the toluidide, was condensed with sulphur monochloride in a similar way. The product separated from acetone, in which it was sparingly soluble, in short needles, melting and decomposing at 202° (Found: $S=26.9$. $C_9H_8O_2N_2S_2$ requires $S=26.66$ per cent.).

Ethyl Dithiomesoxo-p-tolylamate.

Ethyl malono-*p*-tolylamate, prepared by Whiteley's method (*ibid.*, pp. 36, 40) at $120-125^{\circ}$, was condensed (8 grams) with sulphur monochloride (5 grams) in benzene (50 c.c.) in the usual way. The reaction began in the cold, with copious evolution of hydrogen chloride. The liquid was cooled and filtered and the solvent was allowed to evaporate. The semi-solid mass was redissolved in benzene, and solidified when the solution was cooled with ice. It sintered at 74° and melted at 90° (Found: $S=22.44$. $C_{12}H_{13}O_3NS_2$ requires $S=22.61$ per cent.).

Ethyl Dithiomesoxo-o-tolylamate.

This substance was prepared like the *para*-compound and was purified by repeated spontaneous evaporation of its solution in benzene and finally in ether. It melted at 62° (Found: $S=22.48$. $C_{12}H_{13}O_3NS_2$ requires $S=22.61$ per cent.).

Methylmalono-p-toluidide Disulphide (Formula II).

Methylmalono-p-toluidide was prepared from ethyl methylmalonate (9 grams) and *p*-toluidine (10 grams) in the same way as the lower homologue previously mentioned, except that in this case the temperature was 160° rising to 180°. It separated in a very pure condition and after crystallisation from acetic acid melted at 220° (Found : N=9·79. $C_{18}H_{20}O_2N_2$ requires N=9·46 per cent.).

The above amide (8 grams) and sulphur monochloride (2 grams) were allowed to react in benzene (100 c.c.) in the usual manner. The solution was cooled and filtered and the solvent was allowed to evaporate. The residue was again dissolved in benzene and the product was crystallised from a mixture of benzene and light petroleum and then melted at 224—225° (Found : S=10·19. $C_{36}H_{38}O_4N_4S_2$ requires S=9·78 per cent.).

The *dodecanitro*-derivative was obtained by the regulated action of fuming nitric acid and precipitated by the addition of water. At no time should the liquid be allowed to boil. After being filtered and washed with nitric acid and with water, it was obtained as a pale yellow powder decomposing at 140° (Found : N=18·50; S=5·61. $C_{36}H_{26}O_{28}N_{16}S_2$ requires N=18·76; S=5·36 per cent.).

Methylmalono-o-toluidide Disulphide.

Methylmalono-o-toluidide was prepared and purified like the *para*-compound. It melted at 161° (Found : N=9·52. $C_{18}H_{20}O_2N_2$ requires N=9·46 per cent.).

The amide was condensed with sulphur monochloride as in the case of the *para*-compound; the product crystallised from alcohol in mealy crystals which melted at 174° (Found : S=10·09. $C_{36}H_{38}O_4N_4S_2$ requires S=9·78 per cent.).

Methylmalonomono-o-toluidide Disulphide,

Methylmalonomono-o-toluidide was prepared from ethyl methylmalonate (22 grams) and *o*-toluidine (9 grams) in a similar manner as malonomono-*p*-toluidide and was crystallised from dilute alcohol. It separated in pearly scales melting at 117° (Found : N=14·05. $C_{11}H_{14}O_2N_2$ requires N=13·60 per cent.).

This amide (6 grams) was condensed with sulphur monochloride (2 grams) in the presence of benzene (100 c.c.) as in the previous cases. The product was crystallised from a mixture of benzene and light petroleum, when it melted at 207—208° (Found : S=13·95. $C_{22}H_{16}O_4N_4S_2$ requires S=13·50 per cent.).

Methylmalonodimethylamide Disulphide, S₂[CMe(CO·NHMe)]₂.

Methylmalonodimethylamide (Franchimont, *Rec. trav. chim.*, 1885, 4, 204), when condensed (10 grams) with sulphur monochloride (5 grams) in benzene (100 c.c.), yielded a crystalline product which melted at 200° after being washed with benzene (Found : S=18·72. C₁₂H₂₆O₄N₄S₂ requires S=18·28 per cent.).

Interaction of Ethyl Sodiocyanoacetate and Sulphur Monochloride.

Ethyl sodiocyanoacetate, prepared from 25 grams of ethyl cyanoacetate, was refluxed for one hour with sulphur monochloride (15 grams) and dry benzene (100 c.c.). The dark solution on evaporation left an oil which, when distilled under reduced pressure, yielded a solid. After crystallisation from ether, this melted at 117—118°, contained no sulphur and was identified as ethyl dicyanosuccinate (Found : N=12·76. Calc., N=12·50 per cent.).

Interaction of Ethyl Sodiomalonnate and Sulphur Monochloride.

Ethyl sodiomalonnate, prepared from 50 grams of the ester, was refluxed with sulphur monochloride (0·5 mol.) in the manner described in the last experiment. The product, after crystallisation from ether, was identified as ethyl ethanetetra-carboxylate (Found : C=52·46; H=6·57. Calc., C=52·83; H=6·91 per cent.).

Interaction of Ethyl Cyanoacetate and Sulphur Monochloride.

Ethyl cyanoacetate (20 grams) was heated on a water-bath with sulphur monochloride (25 grams) and the product obtained on cooling was extracted from the sulphur produced by a large quantity of ether. The solid obtained after evaporation of the solvent was crystallised from benzene. It melted at 117—118° and was identified as ethyl dicyanosuccinate.

Interaction of Ethyl Malonnate and Sulphur Monochloride.

This condensation was conducted like the preceding, excepting that heating on a sand-bath was necessary to complete the reaction. The solid product was extracted with benzene and crystallised from light petroleum until it melted at 57—58°. It was identified as ethyl ethylenetetra-carboxylate. The same product was obtained when benzene was used as solvent and the product (an oil) subjected to distillation under reduced pressure.

Interaction of 1:1-Dimethylcyclohexane-3:5-dione and Sulphur Monochloride. 3:5:3':5'-Tetraketo-4:4'-bisdithio-1:1:1':1'-tetramethyldicyclohexyl 2:2'-Disulphide (Formula VII).

The ketone (5 grams) and sulphur monochloride (10 grams) were allowed to react in boiling benzene (100 c.c.). The solution on cooling was filtered and the solvent was allowed to evaporate. The residue was again dissolved in benzene and after the solvent had evaporated, crystallised from a mixture of benzene and light petroleum, when it softened at 110° and melted with decomposition at 150°. The molecular weight, determined by the cryoscopic method in benzene solution, was 472.5 (Found : S=40.93. $C_{16}H_{18}O_4S_6$ requires S=41.20 per cent.; M=466).

Interaction of cycloHexanespirocyclohexane-3:5-dione and Sulphur Monochloride. 1:1'-Dicyclohexanespiro-3:5:3':5'-tetraketo-4:4'-bisdithiodicyclohexylene 2:2':6:6'-Bisdisulphide (Formula VIII).

The ketone (2 grams), after being thoroughly dried in the steam-oven for fifteen minutes, was heated under reflux with sulphur monochloride (3 grams) and dry benzene (100 c.c.). The product was isolated and purified in the same way as the preceding compound; it softened at 113° and melted and decomposed at 155°. The molecular weight, determined by the cryoscopic method in benzene solution, was 618 (Found : S=41.72. $C_{22}H_{24}O_4S_8$ requires S=42.10 per cent.; M=608).

Interaction of cycloPentanespirocyclohexane-3:5-dione and Sulphur Monochloride. cycloPentanespiro-3:5-diketo-4-dithiocyclohexane (Formula VI).

The ketone (2 grams) was boiled for two hours with sulphur monochloride (3 grams) dissolved in benzene (50 c.c.). The product was isolated and purified as in the preceding cases; it softened at 114° and melted at 135°. The molecular weight, determined by the cryoscopic method in benzene solution, was 219 (Found : S=28.45. $C_{10}H_{12}O_2S_2$ requires S=28.07 per cent.; M=228).

$\alpha\gamma$ -Disulphidoacetonedicarboxydianilide (Formula X).

The acetonedicarboxydianilide required for the purpose was prepared by the method of Besthorn and Garben (*loc. cit.*) and purified by crystallisation from benzene. The more soluble ethyl γ -phenylcarbamylacetoacetate was recovered as a by-product from the residues.

A mixture of the dianilide (4 grams), sulphur monochloride (4 grams), and dry benzene (100 c.c.) was heated under reflux for two hours. The solution became deep red and hydrogen chloride was immediately evolved. The liquid was allowed to cool and the golden-yellow, crystalline product collected and recrystallised from benzene, when it melted at 220° . The molecular weight, determined by the cryoscopic method in benzene solution, was 343 (Found: $N=8.15$; $S=18.41$. $C_{17}H_{14}O_3N_2S_2$ requires $N=7.82$; $S=17.87$ per cent.; $M=358$).

Ethyl γ -Phenylcarbamyl- $\alpha\gamma$ -bisdisulphidoacetoacetate (Formula IX).

Ethyl γ -phenylcarbamylacetoacetate (4 grams) and sulphur monochloride (5 grams) were heated under reflux with dry benzene (50 c.c.). The red solution was filtered and the solvent allowed to evaporate, the residue being repeatedly dissolved in benzene and precipitated by light petroleum until it was pure. When heated, it sintered at 115° and melted with decomposition at 156 – 157° . The molecular weight, determined by the cryoscopic method in benzene, was 393.5 (Found: $S=34.69$. $C_{13}H_{11}O_3NS_4$ requires $S=34.31$ per cent.; $M=373.0$).

*$\alpha\gamma$ -Disulphidoacetonedicarboxydi-*p*-toluidide.*

*Preparation of Acetonedicarboxydi-*p*-toluidide.*—Acetonedicarboxylic ester (25 grams) and *p*-toluidine (17.5 grams) were heated together in a sealed tube at 120° for twenty-four hours. When the contents of the tube were poured into benzene (500 c.c.) the *toluidide* separated in beautiful crystals, which, after recrystallisation from benzene, melted at 169 – 170° (Found: $N=8.25$. $C_{19}H_{20}O_3N_2$ requires $N=8.64$ per cent.).

A mixture of the amide (6 grams), sulphur monochloride (5 grams), and dry benzene (100 c.c.) was heated under reflux for two hours. The product, being sparingly soluble in benzene, separated from the hot solution in brilliant, golden-yellow flakes which melted on recrystallisation at 216 – 217° (Found: $S=16.14$. $C_{19}H_{18}O_3N_3S_2$ requires $S=16.58$ per cent.).

*$\alpha\gamma$ -Disulphidoacetonedicarboxydi-*o*-toluidide.*

*Preparation of Acetonedicarboxydi-*o*-toluidide.*—This substance was prepared in the same way as the corresponding *p*-tolyl derivative, and on recrystallisation from benzene melted at 167° (Found: $N=8.86$. $C_{19}H_{20}O_3N_2$ requires $N=8.64$ per cent.).

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The amide was heated with sulphur monochloride in the same way as the corresponding *p*-compound. The product was sparingly soluble in benzene, from which it separated in brilliant orange crystals melting at 225° with decomposition (Found : S=16.88. $C_{19}H_{18}O_3N_2S_2$ requires S=16.58 per cent.).

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