

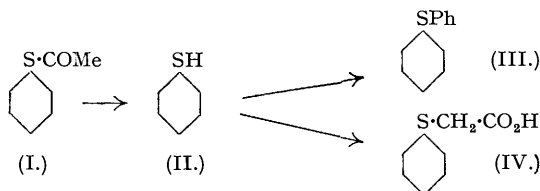
35. The Addition of Thio-compounds to Olefins. Part II. Reactions of Thiolacetic and Mono-, Di-, and Tri-chlorothiolacetic Acids.

By J. I. CUNNEEN.

*cyclo*Hexene, 1-methyl*cyclo*hexene, dihydromyrcene, squalene, and rubber* combine additively with the above named thio-acids, the reactions proceeding similarly to, but more easily than, those reported with thiols in Part I. The parallelism noted previously between the ease of thiol addition and the facility of proton removal from the S-H bond as measured by acidity not only extends to thiol acids generally, but also accords with the fact that among the latter themselves the more acid chloro-substituted compounds are the more active addenda. A reactivity order, *cyclo*hexenes > dihydromyrcene > squalene > rubber, is again apparent, but whereas this serves to make the last olefin inert towards thiols, yet thio-acid adducts are readily prepared, and these are of considerable technological interest as oil- and petrol-resistant rubbers.

SINCE thiol acids are a limited group, it is not surprising that their additive reactivity, $>C:C< + R\cdot CO\cdot SH \longrightarrow >CH\cdot\overset{|}{C}\cdot S\cdot COR$, has been but meagrely explored; in fact, the few such reactions reported have been concerned only with thiolacetic acid. Holmberg (*Arkiv Kemi Min. Geol.*, 1938, 12, B, No. 47) provided the first example in the preparation of β -phenylethyl thiolacetate from styrene in good yield at room temperature. Ipatieff and Friedmann (*J. Amer. Chem. Soc.*, 1939, 61, 71) studied the addition to propylene, *isobutylene*, *isopropylethylene*, and trimethylethylene at various temperatures and found that, although propylene was inert, the other olefins gave thiolacetates in high yield, the orientation of addition being contrary to Markownikoff's rule. From a comparison of the reactivities of ethanethiol, thiophenol, and thiolacetic acid towards propylene and *isobutylene*, these authors concluded that the last is a less active addendum than the thiols. Sjöberg (*Ber.*, 1941, 74, 64) treated allyl chloride with the thiol acid at 160°, isolated γ -chloropropyl thiolacetate, and converted this ester into the corresponding thiol by hydrolysis with methyl-alcoholic hydrogen chloride. The addition to some unsaturated acids was followed by Holmberg and Schjönberg (*Arkiv Kemi Min. Geol.*, 1940, 14, A, No. 7), who confirmed Ipatieff and Friedmann's observations concerning the "abnormal" orientation. The present work describes the reaction with *cyclo*hexene, 1-methyl*cyclo*hexene, dihydromyrcene, squalene, and rubber of thiolacetic and mono-, di- and tri-chlorothiolacetic acids, the last two acids being specially synthesised.

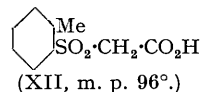
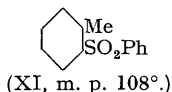
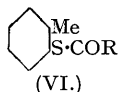
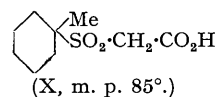
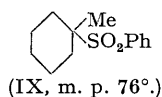
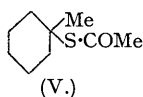
Reactions with Thiolacetic Acid.—On mixing this acid with the liquid olefins named above a violent reaction occurred with the evolution of much heat. The *cyclo*hexene reaction product, isolated by distillation at reduced pressure, was characterised as *cyclohexyl thiolacetate* (I) in the following way. Alkaline hydrolysis gave the thiol (II), whose sodium salt reacted with iodobenzene and with bromoacetic acid to give *cyclohexyl phenyl sulphide* (III) and *cyclohexyl-*



thioglycollic acid (IV), respectively, which are readily identified by means of their crystalline sulphones (see Part I). 1-Methyl*cyclo*hexene gave an analogous product which could be either the "normal" (V) or the "abnormal" (VI, R = Me) ester. Again, the product was hydro-

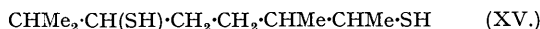
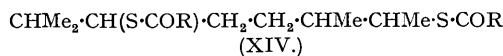
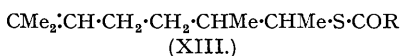
* British and U.S. Patent Specifications pending.

lysed to the *thiol* (VII or VIII), and this converted into the corresponding phenyl sulphide and thioglycollic acid, which were oxidised to the respective crystalline sulphones, m. p. 108° and 96°. The alternative compounds, (IX) and (X) or (XI) and (XII), have been unambiguously

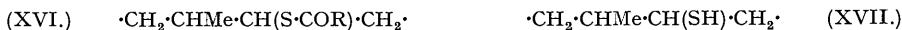


differentiated in Part I so that m. p. and mixed m. p. data establish with certainty that the sulphones now obtained are (XI) and (XII), and thus that the original ester is (VI, R = Me).

Dihydromyrcene gave two liquid *thiolacetates* corresponding to the mono- and di-addition compounds (XIII and XIV, R = Me), the latter being readily hydrolysed with alcoholic alkali to the *dithiol* (XV). The squalene reaction *product* when freed from excess of thiol acid in a high



vacuum was a colourless viscous oil in which 36% of the double bonds had reacted. Reaction between rubber and the thiol acid was investigated in benzene solution. On irradiating such a solution contained in "Pyrex" vessels with a mercury-vapour lamp for a few hours and precipitating the *product* with excess alcohol, a white rubber-like material was obtained in which almost quantitative addition of the thiol acid fragments to the double bonds of the rubber had occurred. The irradiation conditions described appear to be essential for facile reaction. Illumination with a tungsten-filament lamp, heating the reactants to 100—130° in a Carius tube, and leaving a benzene solution in the light of the laboratory for as long as 2 years, in the presence or absence of ascaridole in each case, only induced a fractional amount of the thiol acid to combine. Irradiation with a carbon arc was more successful, but still considerably less efficient than the mercury-vapour lamp. The almost fully saturated rubber derivatives physically resembled the original rubber and gave no detectable indications of cross-linking or molecular degradation. Just as with the simpler olefin analogues, the *rubber thiolacetate* could be hydrolysed to a *thiol*, isolated as a hard fibrous substance. It



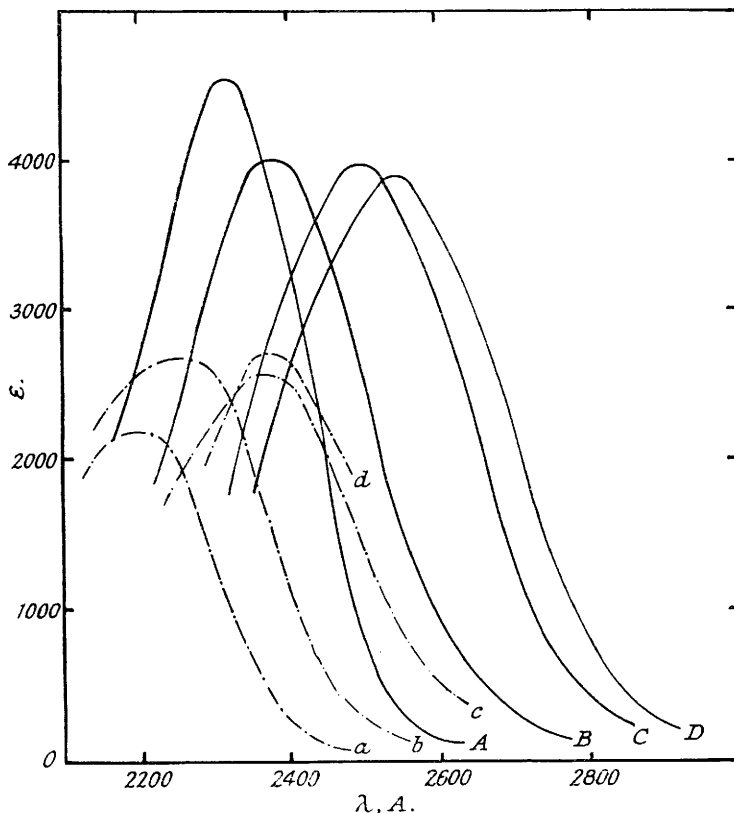
seems certain that the reaction proceeds similarly with all the olefins considered, and therefore that (XVI, R = Me) represents the repeating unit in rubber thiolacetate and (XVII) that in *rubber thiol*, a decision which is confirmed by ultra-violet absorption measurements.

Reactions with Monochlorothioloacetic Acid.—The vigorous reactions of the parent acid with the liquid olefins were repeated with this acid, colourless liquid addition products being obtained in almost quantitative yield. A novel feature of this series, however, is that alkaline hydrolysis of the chlorothioloacetate produces, not thiols, but substituted thioglycollic acids; *e.g.*, cyclohexyl chlorothioloacetate gives cyclohexylthioglycollic acid, obviously owing to interaction between the thiol and chloroacetic acid, the primary hydrolysis products: $\text{C}_6\text{H}_{11}\cdot\text{S}\cdot\text{CO}\cdot\text{CH}_2\text{Cl}$ ($\text{C}_6\text{H}_{11}\cdot\text{SH} + \text{CH}_2\text{Cl}\cdot\text{CO}_2\text{H}$) \longrightarrow $\text{C}_6\text{H}_{11}\cdot\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$. Oxidation of the derived thioglycollic acid to its crystalline sulphone of known constitution (Part I) serves to identify the mode of addition to the unsymmetrical olefinic centre in 1-methylcyclohexene, and proves that addition proceeds abnormally to give the *ester* (VI, R = CH_2Cl). Dihydromyrcene again gave *mono-* and *di-*adducts (XIII and XIV, R = CH_2Cl), the former separable as a pure compound, but squalene, although reacting vigorously, yielded incompletely saturated products.

In marked contrast to thiolacetic acid, monochlorothioloacetic reacts readily with rubber in benzene solution in the presence of ascaridole in the dark. Irradiation with the mercury-vapour lamp accelerates the reaction considerably, but even so the most convenient preparative method is to leave a solution as intimated above in ordinary daylight for a few days and then to precipitate the rubber derivative either with excess of alcohol or following removal of the benzene by steam distillation. The nature of the peroxide catalyst is somewhat critical. Without added peroxide the reaction is extremely slow; benzoyl peroxide is an almost ineffective pro-

moter, *tert.*-butyl hydroperoxide is much better, but not nearly so good as ascaridole. By limiting the extent of addition a whole series of rubber chlorothiolacetates can be obtained varying from slightly modified rubber to the almost fully saturated hard solid. From the point of view of possible commercial value, the most interesting derivatives were those in which about three-quarters of the double bonds had been saturated: they possess elastic properties comparable with those of the original rubber, are thermally stable at 140°, and have high resistance to solvents such as light petroleum (absorption practically nil) and aviation fuel (absorption 20—30% for a fuel containing 35% of aromatic hydrocarbons). The nature of the reaction and the properties of the products leave no doubt that monochlorothiolacetic

FIG. 1.



Except where otherwise stated, pure cyclohexane was used as the solvent.

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|--------------------------------|--------------------------------------|
| a, Thiolacetic acid. | A, 2-Methylcyclohexyl thiolacetate. |
| b, Monochlorothiolacetic acid. | B, cycloHexyl chlorothiolacetate. |
| c, Dichlorothiolacetic acid. | C, cycloHexyl dichlorothiolacetate. |
| d, Trichlorothiolacetic acid. | D, cycloHexyl trichlorothiolacetate. |

acid adds to rubber to give an essentially linear polymer with a repeating unit (XVI, $R = CH_2Cl$), and spectrographic data can again be adduced to confirm this view.

Reactions with Dichlorothiolacetic Acid.—Addition to cyclohexene, dihydromyrcene, and squalene occurred with the usual facility. cycloHexyl dichlorothiolacetate, $C_6H_{11}\cdot S\cdot CO\cdot CHCl_2$, failed to yield a thiol on hydrolysis, the product being a high-boiling viscous liquid of indefinite constitution, but almost certainly a mixture of α -chlorocyclohexylthioglycollic acid, $C_6H_{11}\cdot S\cdot CHCl\cdot CO_2H$, and bis-cyclohexylthioacetic acid, $CH(C_6H_{11}S)_2\cdot CO_2H$, which would result from interaction of the initially formed thiol and dichloroacetic acid. Dihydromyrcene gave mono- and di-adducts again (XIII and XIV, $R = CHCl_2$), of which only the former could be fully purified by distillation. From squalene was obtained an almost colourless gum whose analysis indicated about 75% addition. Rubber reacted just as with monochlorothiolacetic acid, derivatives of varying dichlorothiolacetate content being prepared by leaving benzene

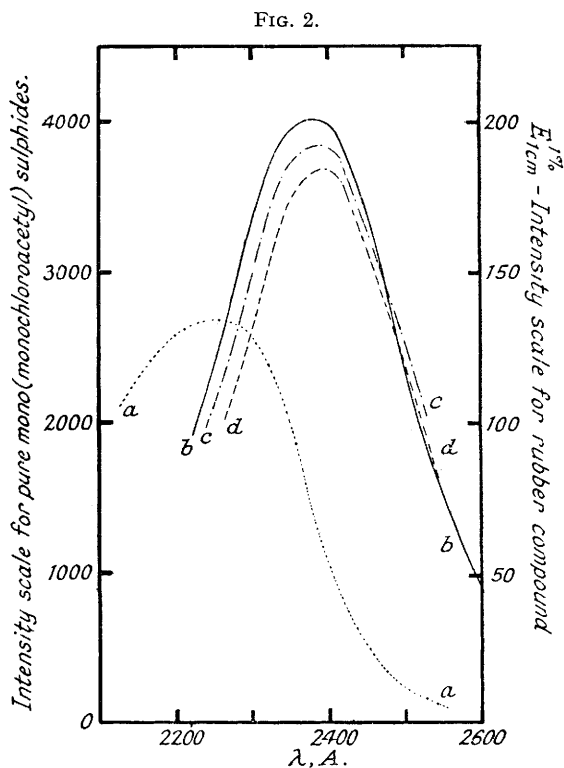
solutions of the reactants plus a little ascaridole in the dark at room temperature for periods varying up to 15 days. The products, undoubtedly containing the units (XVI, R = CHCl₂), were slightly harder and less elastic than similarly saturated monochlorothioacetates.

Reactions with Trichlorothiolicetic Acid.—This acid was added to cyclohexene, 1-methylcyclohexene, dihydromyrcene, and rubber, trichlorothiolicetates being formed readily in each case. Methylcyclohexyl trichlorothiolicetate was identified as (VI, R = CCl₂) by careful hydrolysis, to a thiol which reacted with iodobenzene to give a phenyl sulphide, this yielding in turn on oxidation the sulphone (XI). Rubber reacted readily in the dark under peroxidic conditions, and more rapidly on irradiation with ultra-violet light. Following the trend described from the monochloro- to the dichloro-thioacetates, the products were still harder for similar extents of additions, the almost saturated compounds being tough thermoplastic materials resembling gutta-percha.

Absorption Spectra.—In agreement with the spectra of some simple acetyl sulphides already reported in the literature (Sjöberg, *Z. physikal. Chem.*, 1942, B, 52, 909), the ultra-violet absorption curves of the four thioacids and their cyclohexyl esters shown in Fig. 1 are characterised by intense absorption near 2300 Å. ($\epsilon = 3800$), which is evidently associated with conjugation between the carbonyl double bond and the unshared valency electrons of the sulphur atom, as will be more fully discussed elsewhere by H. P. Koch. As the acetyl hydrogen atoms are replaced by chlorine, both acids and esters display successive red shifts that are sufficiently marked to be characteristic of the degree of substitution. The acids absorb relatively less (as regards both wave-length and intensity) than the analogous esters, but the identical spectral type of the two series is in agreement with the infra-red absorption evidence (Sheppard and Sutherland, private communication) that thiolacetic acid has the acetyl hydrogen sulphide structure, CH₃·CO·SH. Comparison of the spectra of the esters prepared from cyclohexene and dihydromyrcene, illustrated in Fig. 2 for the monochlorothiolicetate, and data for the other esters presented in the experimental section, show that both position and intensity of the bands are practically independent of the nature of the hydrocarbon radical attached to the sulphur atom.

It is therefore possible to identify and to estimate the composition of the esters obtained from spectroscopically pure rubber by noting the position of the band head and comparing the maximum intensity with the standard intensity of the appropriate $\cdot\text{CH}_2\cdot\text{CHMe}\cdot\text{CH}(\text{S}\cdot\text{CO}\cdot\text{CX}_2)\cdot\text{CH}_2\cdot$ unit (X = H or Cl) as derived from the dihydromyrcene adducts (cf. Fig. 2). Such estimations are found to be in reasonable agreement with the results of elementary microanalysis, thus providing a further example of the value of this spectrographic method for both qualitative and quantitative analysis of complex products resulting from the addition of chromophoric groups to rubber and related olefins (cf. Cunneen, Farmer, and Koch, *J.*, 1943, 472).

Discussion.—The additive reactivity of the thiol acids exactly parallels that displayed by the thiols considered in Part I, which have in common the scission of the thio-compound at the S-H bond, the addition of the fragments contrary to Markownikoff's orientation rule, and the marked response to peroxide catalysis. However, the thiol acids are definitely the more powerful reactants, as shown by the vigour of their reactions with the simpler olefins and by their ability to combine with rubber, which seems beyond the power of the thiols. This fact agrees



a, Monochlorothiolicetic acid. *b*, cycloHexyl chlorothiolicetate. *c*, Dihydromyrcene chlorothiolicetate (in dioxan). *d*, Rubber chlorothiolicetate (in dioxan).

with the rough correlation pointed out in Part I between the activity of the addenda and the dissociation facility of the S-H links as measured by the acidity of the thio-compound. The correlation, which is completely at variance with Ipatieff and Friedmann's deduction (*loc. cit.*), noticeably extends to the thiol acids series itself in that thiolacetic acid requires added activation by ultra-violet light in order to combine with rubber whereas with the stronger chloro-thiolacetic acids combination proceeds readily without this stimulus.

The decrease in reactivity in the olefin series from the cyclohexenes to rubber noted in the thiol reactions is again apparent in the reactions with the thiol acids, although the absolute reaction rates are widely different in the two cases. Attempts to trace the basis of this varying olefinic reactivity form the subject of further investigations in these laboratories.

Thiol acid addition clearly provides a very general method of introducing a substituent R contained in the group $\cdot\text{S}\cdot\text{CO}\cdot\text{CR}$ into an olefin, and in some cases an easy preparation of thiols and derived thio-compounds such as sulphones. The mild reaction conditions, the absence of side reactions, and the ready control of the extent of addition, are particularly valuable when introducing substituents into long-chain olefins such as rubber with the object of modifying some properties (*e.g.*, resistance to solvents) and at the same time maintaining the high-molecular character responsible for the elastic properties. The extreme susceptibility of rubber to molecular degradation on a scale minute chemically but so often substantial physically, which is such a real barrier to useful modification, appears to have been effectively circumvented in the examples now presented.

EXPERIMENTAL.

Thiolacetic Acid Derivatives.

Preparation of Thiolacetic Acid.—Clarke and Hartmann's method (*J. Amer. Chem. Soc.*, 1924, **46**, 1731) was improved by using sulphuric acid as a catalyst instead of acetyl chloride or bromide, and by separating the thiol acid by distillation through an efficient Fenske column. Light absorption in cyclohexane: λ_{max} , 2190 Å. ($\epsilon = 2200$).

Reaction of cycloHexene with Thiolacetic Acid.—A vigorous exothermic reaction occurred on shaking the acid (15.2 g.) with cyclohexene (16.4 g.). After 15 mins., traces of unchanged reactants were removed by distillation at 50° under reduced pressure (water pump). The residue (29.2 g.) was cyclohexyl thiolacetate (I), b. p. 90°/14 mm. (Found: C, 60.1; H, 8.8; S, 20.2. $\text{C}_8\text{H}_{14}\text{OS}$ requires C, 60.6; H, 8.9; S, 20.3%).

cycloHexanethiol (II). The above ester (20 g.), ethyl alcohol (100 c.c.), and 20% aqueous potassium hydroxide (100 c.c.) were refluxed together for 15 mins. The cooled solution was acidified (acetic acid), and the precipitated thiol collected *via* its ethereal solution and distilled. It (11.4 g.) had b. p. 157°/763 mm. (Found: C, 62.0; H, 10.55; S, 27.9. Calc. for $\text{C}_6\text{H}_{12}\text{S}$: C, 62.1; H, 10.3; S, 27.6%).

cycloHexyl phenyl sulphide (III). The above thiol (4.6 g.) was dissolved in ethyl alcohol (30 c.c.), and sodium (0.9 g.) added in small pieces. When all the metal had dissolved the alcohol was removed under reduced pressure, leaving solid cyclohexyl sodium sulphide. To this solid, iodobenzene (8.1 g.) and powdered copper (0.05 g.) were added, and the mixture was heated in an oil-bath at 220° for 2 hours. Ether extraction of the cooled mixture gave cyclohexyl phenyl sulphide, b. p. 97—98°/0.05 mm. (Found: C, 75.0; H, 8.4; S, 16.6. Calc. for $\text{C}_{11}\text{H}_{16}\text{S}$: C, 75.0; H, 8.3; S, 16.65%); its identity was confirmed by oxidation by the standard procedure (see Part I) to cyclohexyl phenyl sulphone, m. p. 74°.

cycloHexylthioglycollic acid (IV). The thiol (II) (4.0 g.) was dissolved in a mixture of ethyl alcohol (22.8 c.c.), potassium hydroxide (1.8 g.), and water (1.2 c.c.), and the solution refluxed under nitrogen. An exactly equivalent solution of bromoacetic acid (4.4 g.) in 50% aqueous ethyl alcohol (19 c.c.) was gradually added, and boiling continued for 4 hours. The mixture was then concentrated to dryness, the solid boiled in water (100 c.c.) for 15 mins., excess of hydrochloric acid added, and the boiling continued for a further 10 mins. The precipitated oil, isolated by chloroform extraction, was the acid (IV) (4.8 g.), b. p. 136°/0.2 mm. (Found: C, 55.0; H, 8.25; S, 18.15; equiv., 180. Calc. for $\text{C}_8\text{H}_{14}\text{O}_2\text{S}$: C, 55.2; H, 8.05; S, 18.4%; equiv., 174), again identified by oxidation to its sulphone, m. p. 82° (cf. Part I).

Reaction of 1-Methylcyclohexene with Thiolacetic Acid.—The olefin (9.6 g.) reacted vigorously with the acid (7.6 g.) to give 2-methylcyclohexyl thiolacetate (VI, R = Me), b. p. 110°/14 mm. (16.2 g.) (Found: C, 62.45; H, 9.3; S, 19.0. $\text{C}_9\text{H}_{16}\text{OS}$ requires C, 62.75; H, 9.3; S, 18.6%). Light absorption in cyclohexane: λ_{max} , 2315 Å. ($\epsilon = 4500$).

2-Methylcyclohexanethiol (VIII). Hydrolysis of the above ester (7 c.c.) as described for the corresponding cyclohexyl homologue gave the thiol (4.25 g.), b. p. 165° (Found: C, 64.2; H, 10.7; S, 24.8. $\text{C}_7\text{H}_{14}\text{S}$ requires C, 64.6; H, 10.8; S, 24.6%).

2-Methylcyclohexyl phenyl sulphide. Prepared from the above thiol and iodobenzene as described for the cyclohexyl derivative, this sulphide had b. p. 108°/0.05 mm. (Found: S, 15.2. Calc. for $\text{C}_{13}\text{H}_{18}\text{S}$: S, 15.55%), and readily yielded the corresponding sulphone, m. p. 108°, on oxidation.

2-Methylcyclohexylthioglycollic acid. This sulphide was prepared by treating the thiol (VIII) with bromoacetic acid in the manner previously described, b. p. 130°/0.05 mm. (Found: C, 57.6; H, 8.8; S, 16.7. Calc. for $\text{C}_9\text{H}_{16}\text{O}_2\text{S}$: C, 57.4; H, 8.4; S, 17.0%). Oxidation gave the acid sulphone, m. p. 96°.

Reaction of Dihydromyrcene with Thiolacetic Acid.—(a) The olefin (8 g.) was shaken for 30 mins. with the quantity of thio-acid (4.4 g.) required to saturate one double bond. Fractional distillation of the oil so obtained gave: (i) unchanged reactants containing a little sulphide, b. p. <100°/12 mm. (1.6 g.); (ii) dihydromyrcene monothiolacetate (XIII, R = Me), b. p. 128°/10 mm. (4.7 g.) (Found: C, 67.35;

H, 10.35; S, 14.6. $C_{12}H_{22}OS$ requires C, 67.3; H, 10.3; S, 14.95% [light absorption in cyclohexane: λ_{\max} , 2315 Å. ($\epsilon = 4750$); in dioxan, λ_{\max} , 2330 Å. ($\epsilon = 4600$)]; (iii) a mixture of the mono- and di-adducts, b. p. 100—122°/0.1 mm. (2.7 g.).

(b) The reaction was repeated but with excess of thiolacetic acid (17 g., with 14 g. of hydrocarbon). The product on fractionation gave: (i) unchanged reagents, b. p. <80°/0.1 mm. (1.6 g.); (ii) *dihydromyrcene bithiolacetate* (XIV; R = Me) containing a trace of the monoacetate, b. p. 110—113°/0.1 mm. (4.2 g.) (Found: C, 58.2; H, 9.05. $C_{14}H_{26}O_2S_2$ requires C, 57.85; H, 8.95%); (iii) *dihydromyrcene bithiolacetate*, b. p. 125°/0.05 mm. (17.8 g.) (Found: C, 57.9; H, 9.0; S, 21.75. $C_{14}H_{26}O_2S_2$ requires C, 57.85; H, 8.95; S, 22.05%) [light absorption in cyclohexane: λ_{\max} , 2315 Å. ($\epsilon = 4750$); in dioxan, λ_{\max} , 2330 Å. ($\epsilon = 4400$)]; (iv) residue (4.1 g.).

Dihydromyrcenethiol (XV). The ester (XIV, R = Me) on alkaline hydrolysis in the usual way gave the parent *dithiol*, a colourless oil, b. p. 128°/25 mm. (Found: C, 58.7; H, 10.6; S, 30.3. $C_{10}H_{22}S_2$ requires C, 58.2; H, 10.7; S, 31.1%).

Reaction of Squalene with Thiolacetic Acid.—The hydrocarbon (2 g.) shaken with the acid (2 g.) for 30 mins. produced a reaction rather less exothermic than that with cyclohexene. Unreacted thiolacetic acid was removed at 100°/10⁻⁵ mm., leaving a colourless viscous syrup (Found: S, 12.05. Calc. for 36% addition: S, 12.05%).

Reaction of Rubber with Thiolacetic Acid.—(i) Three Pyrex tubes (diam. 1.5 cm.), each containing sol rubber (1 g.), benzene (25 c.c.), and thiolacetic acid (1 c.c.), were sealed in a vacuum, placed 6 in. from a mercury-vapour lamp, and irradiated for 4, 8, and 16 hours, severally. The products isolated by precipitation with ethyl alcohol were similar white rubbers (Found, respectively: C, 71.8; H, 10.1; S, 11.85; C, 69.8; H, 9.8; S, 14.2; C, 67.7; H, 9.55; S, 15.1. 50% addition requires C, 68.0; H, 9.45; S, 15.1%).

(ii) A reaction mixture containing more thio-acid (2.5 c.c.) was irradiated for 6 hours with ultra-violet light, and the product isolated as before (Found: S, 15.5. Calc. for 52% addition: S, 15.5%). Light absorption in dioxan: λ_{\max} , 2330 Å., $E_{1\text{cm}}^{1\%} = 205$; $[C_8H_8CH_3CO\text{-SH}]_n$ requires $E_{1\text{cm}}^{1\%} = 10 \epsilon/\text{unit}$ $M = 10 \times 4500/144 = 310$; hence amount of addition is 48%.

(iii) An exactly similar reaction mixture to that used in (ii) was irradiated with the mercury-vapour lamp for 16 hours. The product was a hard white solid (Found: C, 58.95; H, 9.0; S, 20.7. Calc. for 86% addition: C, 60.3; H, 8.6; S, 20.7%).

(iv) The reaction mixture as used in (i) was illuminated for 16 hours with a 300-watt tungsten-filament lamp. A white rubber resulted superficially indistinguishable from the starting material (Found: S, 0.6%, corresponding to 1.3% addition).

(v) The reaction mixture as in (i) but containing ascaridole (0.025 g.) was sealed under vacuum and heated in a Carius furnace at 130° for 3 hours. The rubber product again showed little change (Found: S, 1.5%).

(vi) A reaction mixture as in (v) was sealed under vacuum and left in the light of the laboratory for 1½ years. The product showed 26% addition (Found: S, 9.5. Calc.: S, 9.5%).

(vii) The reaction mixture as used in (i) was illuminated with a carbon arc for 45 hours (Found: C, 69.96; H, 9.9; S, 12.8%, corresponding to 39% addition).

(viii) Some experiments were conducted on a larger scale using an annular form of apparatus (external diam. 6 cm., internal diam. 3.5 cm., length 25 cm.) in which the ultra-violet lamp was suspended, the reaction mixture being sealed under vacuum in the outer jacket and cooled with a rapid stream of water. Milled rubber (M , 150,000) enabled more concentrated solutions to be used. Rubber (15 g.), dissolved in benzene (150 c.c.) containing thiolacetic acid (15 c.c.), irradiated in a vacuum under these conditions for 9 hours, yielded a white rubber (23 g.) (Found: S, 15.7. Calc. for 53% addition: S, 15.7%). A repeat experiment using 25 c.c. of the acid gave 76% addition (Found: C, 61.8; H, 8.8; S, 19.3. Calc.: C, 62.0; H, 8.8; S, 19.3%).

Rubber thiol (XVII). Finely cut *thiolacetyl rubber* (1 g.) (Found: C, 67.7; H, 9.55; S, 15.1. $C_{12}H_{20}OS$ requires C, 68.0; H, 9.45; S, 15.1%) was dissolved in benzene (35 c.c.) and ethyl alcohol (10 c.c.) containing sodium (0.01 g.). The mixture was shaken for 6 hours at room temperature and then poured into excess ethyl alcohol. The *thiol* was precipitated as a fibrous white solid which was thoroughly washed with water (Found: S, 18.7. $C_{10}H_{18}S$ requires S, 18.8%).

Monochlorothiolacetic Acid Derivatives.

Reaction of cyclohexene with Chlorothiolacetic Acid.—The acid (22 g.) [b. p. 48°/16 mm. (Arndt and Berkir, *Ber.*, 1930, **63**, 2390). Light absorption in cyclohexane: λ_{\max} , 2255 Å. ($\epsilon = 2650$)] when added to cyclohexene (17 g.) produced an immediate and vigorous exothermic reaction. The product, when freed from starting materials by heating at 90°/14 mm., was *cyclohexyl chlorothiolacetate*, b. p. 132°/14 mm. (Found: C, 49.95; H, 6.85; S, 16.4; Cl, 18.4. $C_8H_{14}OClS$ requires C, 49.8; H, 6.75; S, 16.6; Cl, 18.4%). Light absorption in cyclohexane: λ_{\max} , 2380 Å. ($\epsilon = 4000$).

Hydrolysis of cyclohexyl chlorothiolacetate. The ester (6.75 g.), ethyl alcohol (35 c.c.), and 20% aqueous potassium hydroxide were refluxed for 4 hours, and after the procedure described for the corresponding thiolacetate, *cyclohexylthioglycolic acid* (5.3 g.) readily separated, b. p. 120°/0.1 mm. (Found: C, 55.25; H, 8.3; S, 18.25; equiv., 178. Calc. for $C_8H_{14}O_2S$: C, 55.2; H, 8.05; S, 18.4%; equiv., 174). This specimen gave the authentic sulphone, m. p. 82°, on oxidation.

Reaction of 1-Methylcyclohexene with Chlorothiolacetic Acid.—Reaction between the hydrocarbon (9.6 g.) and the acid (11 g.) proceeded vigorously to give *2-methylcyclohexyl chlorothiolacetate* (VI, R = CH_2Cl), b. p. 137°/11 mm. (18.7 g.) (Found: S, 14.85; Cl, 18.5. $C_9H_{16}OClS$ requires S, 15.5; Cl, 17.2%).

Hydrolysis of 2-methylcyclohexyl chlorothiolacetate. The ester, hydrolysed as described for the cyclohexene derivative, gave 2-methylcyclohexylthioglycolic acid, b. p. 129°/0.05 mm. (Found: C, 57.45; H, 8.65; S, 16.95; equiv., 184. Calc. for $C_9H_{16}O_2S$: C, 57.4; H, 8.4; S, 17.0%; equiv., 186), identified by its crystalline sulphone, m. p. 96°.

Reaction of Dihydromyrcene with Chlorothiolicetic Acid.—The hydrocarbon (10 g.) was shaken with the acid (5.5 g.) for 15 mins. Distillation of the product gave the following fractions: (i) unchanged reactants, b. p. <100°/14 mm. (3.7 g.); (ii) *dihydromyrcene chlorothiolicetate* (XIII, R = CH₂Cl), b. p. 99°/0.1 mm. (9.2 g.) (Found: C, 57.35; H, 8.4; S, 12.7; Cl, 13.65. C₁₂H₂₁OClS requires C, 58.1; H, 8.6; S, 12.4; Cl, 14.2%) [light absorption in dioxan: λ_{\max} , 2385 Å. ($\epsilon = 3850$)]; (iii) mainly dihydromyrcene bischlorothiolicetate contaminated with some of the mono-adduct, b. p. 108–174°/0.1 mm. (Found: C, 49.8; H, 7.0; Cl, 19.0. Calc. for mixture of 77% di-adduct and 23% mono-adduct: C, 49.4; H, 7.1; Cl, 18.5%).

Reaction of Squalene with Chlorothiolicetic Acid.—Squalene (10 g.) was shaken with the acid (17 g.) for 30 mins., the exothermic reaction then having ceased. Unreacted acid was removed in a vacuum (10⁻⁵ mm.) at 100° leaving a pale green, viscous syrup evidently consisting of a mixture of squalene chlorothiolicetates (Found: S, 15.8; Cl, 17.2. Calc. for 74% addition: S, 15.8; Cl, 17.3%).

Reaction of Rubber with Chlorothiolicetic Acid.—The following are a representative selection of the many experiments carried out with rubber and this acid. (i) A solution of sol rubber (1 g.), benzene (25 c.c.), monochlorothiolicetic acid (1.5 c.c.), and ascaridole (0.05 g.) was sealed under vacuum and illuminated for 6 hours with the mercury-vapour lamp. The product precipitated by ethyl alcohol was a hard white solid (2.2 g.) (Found: C, 48.7; H, 6.6; S, 17.1; Cl, 19.0. Calc. for 88% addition: C, 49.1; H, 6.4; S, 17.1; Cl, 19.0%). (ii) A reaction mixture similar to that used in (i) was evacuated and left in the dark at room temperature for 7 days. The product showed only 58.5% addition (Found: S, 13.75; Cl, 15.6. Calc.: S, 14.1; Cl, 15.65%). Light absorption in dioxan, λ_{\max} , 2390 Å., $E_{1\text{cm}}^{1\%} = 180$. [C₅H₈Cl·CH₂·CO·SH]_n requires $E_{1\text{cm}}^{1\%} = 10\epsilon/\text{unit } M = 10 \times 3850/178.5 = 216$, and hence amount of addition is 65.5%. Imbibition of aviation fuel*, 40%. (iii) Five tubes each containing milled rubber (M , 150,000) (1 g.), benzene (10 c.c.), monochlorothiolicetic acid (1 c.c.), and ascaridole (0.05 g.) sealed in a vacuum were kept at room temperature for 4, 6, 10, 18 and 34 days, severally. The products were precipitated and dried, and then had the properties and analytical values given in the table. (iv) The catalytic activity of different peroxides was investigated as follows. To one of four tubes containing the basic reaction mixture as in (iii) was added ascaridole, to another benzoyl peroxide, to the third *tert.*-butyl hydroperoxide, and no addition was made to the fourth. These tubes were sealed under vacuum and kept at room temperature in the dark for 4 days.

The amounts of aviation fuel imbibed by the respective products, isolated in each case by alcohol precipitation, are shown in the table, and since the imbibition varies inversely as the extent of thio-acid addition the catalytic activities of the various peroxides in promoting this addition are clearly seen. Other series of experiments carried out with different peroxide concentrations all showed the same order.

Reaction time, days.	Catalyst.	S, %.	Cl, %.	Liquid imbibed, %.	
				Light petroleum (b. p. 40–60°).	Aviation fuel.
4	Ascaridole	12.5	14.3	5	53
6	"	13.1	15.1	2	43
10	"	15.5	17.4	1	36
18	"	15.9	18.0	—	27
34	"	16.0	17.9	—	24
4	"	12.5	14.3	5	53
4	(None)	—	—	—	(Product dissolved)
4	Benzoyl peroxide	—	—	—	190
4	<i>tert.</i> -Butyl hydroperoxide	—	—	—	72

(v) Larger-scale experiments were carried out in the following way. Milled rubber (50 g.) was dissolved in benzene (500 c.c.) containing monochlorothiolicetic acid (36 c.c.) and ascaridole (2.5 c.c.), and the solution kept in the absence of air at room temperature and in the dark for 15 days. After removal of the benzene by steam-distillation, the product which separated was washed with ethyl alcohol and dried (Found: C, 56.45; H, 7.3; S, 13.2; Cl, 15.3. Calc. for 56% addition: C, 56.0; H, 7.4; S, 13.8; Cl, 15.3%). Imbibition of aviation fuel, 50%.

Dichlorothiolicetic Acid Derivatives.

Preparation of Dichlorothiolicetic Acid.—Arndt and Berkir's method (*loc. cit.*) for the preparation of monochlorothiolicetic acid was adapted to the present synthesis. A rapid stream of dry hydrogen sulphide was passed through a cooled (0°), well-stirred solution of dichloroacetyl chloride (500 g.) and powdered dry aluminium chloride (10 g.) until the evolution of hydrogen chloride had ceased (6–7 hours). Distillation of the reaction mixture yielded *dichlorothiolicetic acid* as a pale green liquid, b. p. 56°/16 mm. (315 g.) (Found: C, 16.55; H, 1.8; S, 21.65; Cl, 49.4. C₂H₂OCl₂S requires C, 16.55; H, 1.4; S, 22.05; Cl, 48.9%). Light absorption in cyclohexane: λ_{\max} , 2365 Å. ($\epsilon = 2550$).

Reaction of cycloHexene with Dichlorothiolicetic Acid.—The usual reaction between the hydrocarbon (25 g.) and the thio-acid (42 g.) proceeded on shaking, *cycloHexyl dichlorothiolicetate* was obtained as the sole product, b. p. 148°/12 mm. (63 g.) (Found: C, 42.4; H, 5.5; Cl, 31.9. C₈H₁₂OCl₂S requires C, 42.3; H, 5.3; Cl, 31.3%). Light absorption in cyclohexane: λ_{\max} , 2495 Å. ($\epsilon = 3950$). Hydrolysis with alcoholic alkali afforded an unidentified viscous oil, b. p. >220°/758 mm. No cyclohexanethiol could be isolated.

Reaction of Dihydromyrcene with Dichlorothiolicetic Acid.—The hydrocarbon (8 g.) was shaken for

* Aviation Fuel RDEF/75 containing approximately 35% of aromatic hydrocarbons was used for imbibition tests.

15 mins. with the thio-acid (12 g.). Fractional distillation of the oily product gave: (i) unchanged reactants containing a little acetate, b. p. $<100^{\circ}/0.1$ mm. (2.5 g.); (ii) *dihydromyrcene dichlorothioliacetate* (XIII, R = CHCl_2) (4.6 g.), b. p. $118^{\circ}/0.1$ mm. (Found: S, 11.3; Cl, 25.1. $\text{C}_{12}\text{H}_{20}\text{OCl}_2\text{S}$ requires S, 11.3; Cl, 25.1%) [light absorption in dioxan: λ_{max} , 2505 Å. ($\epsilon = 3900$)]; (iii) a mixture of mono- and di-adducts (0.8 g.), b. p. $160\text{--}180^{\circ}/0.1$ mm. (Found: C, 43.7; H, 5.8; S, 14.2. Calc. for a mixture 38% $\text{C}_{12}\text{H}_{20}\text{OCl}_2\text{S}$ and 62% $\text{C}_{14}\text{H}_{22}\text{O}_2\text{Cl}_2\text{S}_2$: C, 43.7; H, 5.9; S, 13.6%); (iv) residue (12 g.).

Reaction of Squalene with Dichlorothioliacetic Acid.—After the hydrocarbon (2 g.) had been shaken with the thio-acid (4.5 g.) for 30 mins., unreacted acid was removed at $100^{\circ}/10^{-5}$ mm., leaving a pale green gum (Found: C, 43.2; H, 5.6; Cl, 29.55. Calc. for 75% addition: C, 43.8; H, 5.6; Cl, 30.0%).

Reaction of Rubber with Dichlorothioliacetic Acid.—(i) A solution of sol rubber (1 g.), benzene (30 c.c.), ascaridole (0.05 g.), and acid (1.5 c.c.) was sealed under vacuum and left in the dark at room temperature for 10 days. The viscosity of the solution increased almost to the point of gelation. The product obtained by precipitation with ethyl alcohol followed by extraction (Soxhlet) with methyl alcohol in an atmosphere of nitrogen for 24 hours was a white rubber (2.5 g.) (Found: C, 44.4; H, 5.5; S, 13.15; Cl, 29.5. Calc. for 71% addition: C, 44.8; H, 5.5; S, 13.3; Cl, 29.5%). This material showed extensive but sluggish elastic behaviour. (ii) Sol rubber (0.5 g.), benzene (20 c.c.), ascaridole (0.02 g.), and the thio-acid (1.0 c.c.) were kept under vacuum for 5 days at room temperature in the dark. The product isolated in the usual way was a white rubber (Found: S, 10.5; Cl, 23.75. Calc. for 44.4% addition: S, 10.7; Cl, 23.75%).

Trichlorothioliacetic Acid Derivatives.

Preparation of Trichlorothioliacetic Acid.—The acid chloride (500 g.), treated in the usual manner, afforded a mixture which on fractional distillation gave: (i) trichloroacetyl chloride containing some of the thio-acid, b. p. $44\text{--}50^{\circ}/11$ mm. (85 g.); (ii) *trichlorothioliacetic acid*, b. p. $57^{\circ}/11$ mm. (348 g.), an almost colourless liquid (Found: C, 13.4; H, 0.6; S, 17.55; Cl, 59.7. $\text{C}_2\text{HOCl}_3\text{S}$ requires C, 13.4; H, 0.6; S, 17.8; Cl, 59.3%) [light absorption in cyclohexane: λ_{max} , 2375 Å. ($\epsilon = 2700$)]; (iii) residue (43 g.).

Reaction of cycloHexene with Trichlorothioliacetic Acid.—The solution of the olefin (8.2 g.) in the acid (18 g.) was shaken for 15 mins. The resulting oil on distillation gave exclusively cyclohexyl *trichlorothioliacetate*, b. p. $151^{\circ}/12$ mm. (25.1 g.) (Found: C, 36.95; H, 4.3; S, 12.25; Cl, 40.6. $\text{C}_6\text{H}_{11}\text{OCl}_3\text{S}$ requires C, 36.7; H, 4.2; S, 12.25; Cl, 40.75%). Light absorption in cyclohexane: λ_{max} , 2540 Å. ($\epsilon = 3900$).

Reaction of 1-Methylcyclohexene with Trichlorothioliacetic Acid.—2-Methylcyclohexyl *trichlorothioliacetate* (VI, R = CCl_3), b. p. $96^{\circ}/0.1$ mm. (Found: C, 39.65; H, 5.15; S, 11.3; Cl, 38.4. $\text{C}_8\text{H}_{13}\text{OCl}_3\text{S}$ requires C, 39.2; H, 4.7; S, 11.65; Cl, 38.6%), was prepared in almost theoretical yield from the hydrocarbon and the thio-acid just as described for the cyclohexene derivative. Submitted to the hydrolytic procedure described for cyclohexyl thioliacetates, the ester gave an oil which reacted with iodobenzene to give 2-methylcyclohexyl phenyl sulphide, b. p. $105^{\circ}/0.015$ mm. (Found: C, 76.0; H, 8.9; S, 15.3. Calc. for $\text{C}_{13}\text{H}_{16}\text{S}$: C, 75.6; H, 8.75; S, 15.55%), identified by its crystalline sulphone, m. p. 108° .

Reaction of Dihydromyrcene with Trichlorothioliacetic Acid.—Reaction of the hydrocarbon (11 g.) and the thio-acid (10 g.) in the usual way, followed by distillation gave: (i) unreacted dihydromyrcene (0.6 g.), b. p. $<100^{\circ}/15$ mm., (ii) *dihydromyrcene trichlorothioliacetate* (XIII, R = CCl_3) (12.1 g.), b. p. $119^{\circ}/0.05$ mm. (Found: C, 45.45; H, 6.15; S, 9.7; Cl, 33.3. $\text{C}_{12}\text{H}_{19}\text{OCl}_3\text{S}$ requires C, 45.4; H, 6.0; S, 10.1; Cl, 33.6%) [light absorption in dioxan: λ_{max} , 2550 Å. ($\epsilon = 3900$)]; (iii) a mixture of mono- and di-adducts (0.6 g.), b. p. $120\text{--}155^{\circ}/0.05$ mm. (Found: S, 10.25; Cl, 34.5. Calc. for mixture of 90% $\text{C}_{12}\text{H}_{19}\text{OCl}_3\text{S}$ and 10% $\text{C}_{14}\text{H}_{20}\text{O}_2\text{Cl}_2\text{S}_2$: S, 10.45; Cl, 34.5%); (iv) residue (6.4 g.).

Reaction of Rubber with Trichlorothioliacetic Acid.—(i) Sol rubber (1 g.), dissolved in benzene (30 c.c.) containing the thio-acid (1 c.c.) and *i.e.*, insufficient to saturate all the double bonds) and ascaridole (0.05 g.), was sealed under vacuum and kept at room temperature for 15 days. The product, isolated by alcohol precipitation, was a white rubber-like material (2.1 g.) (Found: C, 48.1; H, 5.5; S, 9.4; Cl, 31.7. Calc. for 42.5% addition: C, 48.7; H, 5.8; S, 9.4; Cl, 31.2%). (ii) A similar solution but containing twice the amount of thio-acid was kept for 7 days under similar conditions. The product was a hard white solid (Found: S, 11.95; Cl, 39.8. Calc. for 75.6% addition: S, 11.95; Cl, 39.8%). Light absorption in dioxan: λ_{max} , 2555 Å., $E_{1\text{cm}}^{1\%} = 140$; $[\text{C}_5\text{H}_8\text{CCl}_3\text{CO-SH}]_n$ requires $E_{1\text{cm}}^{1\%} = 10$ ϵ /unit $M = 10 \times 3900/248 = 155$, and hence amount of addition is 72%. (iii) An exactly similar solution to (ii) was sealed under vacuum in a Pyrex tube (diam. 1.5 cm.), placed 6" from the mercury vapour lamp, and irradiated for 6 hours. The product was a hard, brittle solid (Found: C, 36.0; H, 4.1; S, 12.8; Cl, 40.2. Calc. for 87.6% addition: C, 36.0; H, 4.0; S, 12.4; Cl, 41.4%).

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