

8. *The Addition of Thio-compounds to Olefins. Part I. Reactions of Thioglycollic Acid, Thiophenol, and isoPentanethiol.*

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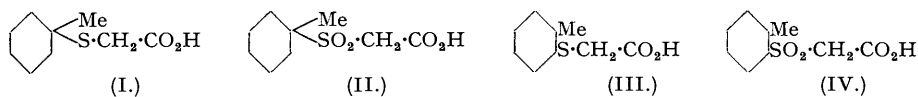
Under peroxidic conditions, *cyclohexene* and 1-methyl*cyclohexene* very readily add the fragments formed by scission of the S-H bonds in the thiols named in the title. At the asymmetrically substituted double bond, the orientation of addition is shown to proceed contrary to Markownikoff's rule. Dihydromyrcene and squalene undergo similar but less vigorous reactions, and rubber does not react.

THE interaction of thiols with unsaturated hydrocarbons was first reported by Posner (*Ber.*, 1905, **38**, 646), who treated thiophenol and benzylthiol with a variety of olefins at room temperature in the presence of acetic and sulphuric acids. With simple olefins, conjugated and non-conjugated, addition of fragments of the thiol produced by scission of the S-H link proceeded readily and, at asymmetrically substituted double bonds, in opposition to Markownikoff's rule: $CR'R''\text{:CHR}''' + \text{SHPH} \longrightarrow \text{CHR}'R''\text{-CH(SPh)R}'''$. More complex non-conjugated olefins (terpinolene and sylvestrene) showed depressed reactivity in that addition occurred at only one double bond, and the highly conjugated systems, stilbene and diphenylbutadiene, failed to react at all. Ashworth and Burkhardt (*J.*, 1928, 1791) confirmed Posner's formulation of the styrene-thiophenol reaction, and pointed out the catalytic activity of sunlight and the inhibition induced by small amounts of piperidine (cf. also Carothers, *J. Amer. Chem. Soc.*, 1933, **55**, 2008). Ipatieff and others (*ibid.*, 1938, **60**, 2731; 1939, **61**, 71) investigated the reaction of thiophenol and ethanethiol with propylene, isobutylene, trimethylethylene, and isopropylethylene at 100–150°, and found that, although addition products "abnormal" with respect to Markownikoff's rule were formed in the absence of catalysts, yet the presence of sulphuric acid, contrary to Posner's findings (*loc. cit.*), reversed the orientation of the addition and led to "normal" products. Contemporaneously, Jones and Reid (*J. Amer. Chem. Soc.*, 1938, **60**, 2452) and Kharasch, Reid, and Mayo (*Chem. and Ind.*, 1938, **57**, 752) showed that traces of peroxides, either as present normally in unsaturated hydrocarbons or as added ascaridole, strongly catalyse the "abnormal" addition, and that quinol effectively impedes the reaction. Mayo and Walling (*Chem. Reviews*, 1940, **27**, 387) have proposed a free-radical chain-reaction mechanism, but kinetic evidence on which to found a detailed reaction scheme is so far lacking.

The object of the present work was the preparation of commercially useful rubber derivatives, since this method, with its apparent specificity of double-bond attack and mild reaction conditions, offers a means of introducing various groups along the chain with a high probability of preserving the molecular character of the original polymer. The only other work along these lines is due to Holmberg (*Ber.*, 1932, **65**, 1349), whose observations of interaction between thioglycollic acid and rubber, balata, and gutta-percha are, however, of dubious significance (see below). This paper records the reactions of thioglycollic, thiophenol, and isopentanethiol with dihydromyrcene (di-isoprene), squalene (a hexaisoprene), and rubber, and with the simple olefins, cyclohexene and 1-methylcyclohexene. Experiments with the latter not only permit unequivocal identification of the reaction products by chemical methods, but serve to emphasize an interesting and surprising variation in reactivity among this series of olefins.

Reactions of Thioglycollic Acid.—Although cyclohexene, 1-methylcyclohexene, and dihydromyrcene are immiscible with the thiol, on shaking equivalent amounts of ordinary laboratory specimens at room temperature a vigorous and highly exothermic reaction occurs immediately. If the olefins were freshly distilled in an atmosphere of nitrogen, reaction was inappreciable, but proceeded almost explosively if a little ascaridole were added. On the other hand, no reaction occurred on mixing squalene with thioglycollic acid containing peroxide, and rubber (which is physically unaffected by the acid) failed to react even under highly favourable peroxidic conditions or irradiation with ultra-violet light.

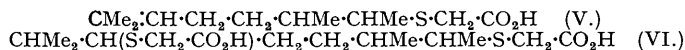
The first three olefins gave liquid addition products in almost the theoretical yields. From cyclohexene was obtained cyclohexylthioglycollic acid, $\text{C}_6\text{H}_{11}\text{S}\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$, characterised by oxidation to the crystalline sulphone, $\text{C}_6\text{H}_{11}\text{SO}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{H}$.



1-Methylcyclohexene gave a corresponding methyl homologue, b. p. 135°/0.1 mm., which can either be the "normal" product (I) or the "abnormal" isomer (III), and which yields a crystalline sulphone, m. p. 96°, on oxidation (*i.e.*, either II or IV). Reaction of 1-methylcyclohexanol with thioglycollic acid under acidic conditions produced a sulphide, which must be (I), oxidizable to the sulphone (II), m. p. 85°, which gave a considerable m. p. depression on admixture with its isomer, m. p. 96°.* The sulphone synthesised *via* the olefin must therefore

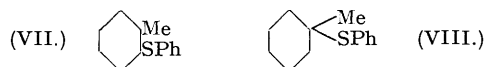
* Since the completion of this work, the abstract appeared (*Chem. Abs.*, 1944, **38**, 3257) of a paper by Hellström and Sandström (*Svensk Kem. Tids.*, 1942, **54**, 149) not yet available in this country. These authors have also carried out the series of reactions leading to the sulphones (II) and (IV), but whereas (II), for which the m. p. 84–85° is given, is correctly designated, a compound, undoubtedly (IV), having m. p. 92–93°, is described as a sulphonic acid.

be (IV), and its parent sulphide the "abnormal" addition product (II). The "normal" sulphide was also obtained by reaction of the olefin and thioglycollic acid in 75% sulphuric acid at 0°, thus supporting Ipatieff's conclusions already mentioned concerning the directive influence of an acidic environment. Dihydromyrcene yielded two liquid *sulphides* corresponding to



the mono-^{*} or di-addition compounds (V) and (VI). The *sulphone* derived from (VI) was analytically pure but failed to crystallise.

Reactions of Thiophenol.—Both *cyclohexenes* and dihydromyrcene, squalene, and rubber dissolve in thiophenol without noticeable evolution of heat. Irradiation of the solution at room temperature with a quartz mercury-vapour lamp for a few hours initiated reaction with the first four olefins and produced high yields of sulphides, but again rubber was almost completely resistant. *cyclohexene* gave the liquid *sulphide*, $\text{C}_6\text{H}_{11}\cdot\text{SPh}$, characterised by the crystalline *sulphone*, $\text{C}_6\text{H}_{11}\cdot\text{SO}_2\text{Ph}$. 1-Methyl*cyclohexene* gave the *sulphide* (VII) whose constitution was established by the non-identity of its derived *sulphone* with that synthesised from



the authentically "normal" *sulphide* (VIII). Ultra-violet absorption also served as a specific criterion for distinguishing the sulphides. The spectrum of (VII), resembling that of *cyclohexyl phenyl sulphide*, has an intense band with a maximum at 2585 Å. ($\epsilon = 7000$) arising from conjugation of the sulphur atom with the adjacent phenyl group. Models show that in (VIII) steric hindrance by the methyl group interferes with the co-planarity of the sulphur valencies and the benzene ring which is essential to full development of such conjugation and, in agreement with this, the associated band is practically absent from the spectrum of (VIII). Analogously to its reaction with the thioglycollic acid, dihydromyrcene yielded a mixture of *mono-* and *di-adducts*. The pale yellow viscous reaction product from squalene was freed from excess of thiol by heating to 100° on a high-vacuum line, and analysis then showed moderate incorporation of thiophenol, but no attempt was made to separate and purify the mixture of phenyl squalene sulphides.†

Reactions of isoPentanethiol.—Irradiation with ultra-violet light of a mixture of *cyclohexene* and the thiol yields the *sulphide* $\text{C}_6\text{H}_{11}\cdot\text{SC}_5\text{H}_{11}$, which can be oxidised to the *sulphone* $\text{C}_6\text{H}_{11}\cdot\text{SO}_2\cdot\text{C}_5\text{H}_{11}$. The corresponding *sulphide* from 1-methyl*cyclohexene* was obtained by heating a mixture of the reagents to 100° for 12 hours, but since the derived sulphone failed to crystallise, it is not possible to prove whether "normal" or "abnormal" addition occurs. A mixture of dihydromyrcene and the thiol, left in daylight at room temperature for a year, gave a mixture of *mono-* and *di-adducts*. Squalene behaved as described for *cyclohexene*, but again rubber remained inert.

Discussion.—The general characteristics of the reactions described above are typical of the peroxide-catalysed additions so extensively explored by Kharasch and his school (for complete list of references, see Mayo and Walling, *loc. cit.*). The most notable feature is the inexplicable reluctance of rubber to react with either of the thiols—the case of thiophenol, an excellent solvent for rubber, effectively disproving any suggestion that insufficient contact of the reactants is responsible, as indeed might be argued with thioglycollic acid. Holmberg's (*loc. cit.*) claim to have obtained reaction with the latter compound by immersing rubber strips for up to two years at room temperature is open to question. According to him, the rubber, completely insoluble at the start, gradually swells and eventually dissolves, forming a homogeneous solution. The author's experience is that small pieces of rubber in excess of the thiol, with or without ascaridole, sealed up in a vacuum and left for two years, are inappreciably swollen, much less dissolved. Holmberg's mixtures presumably had access to air, however, and catalytic activity by oxygen may have promoted the reported addition. On the other hand, thioglycollic acid itself is readily oxidised on atmospheric exposure (Klason, *Ber.*, 1881, 14, 410) so that reactions secondary to this may have initiated the observed changes. The

* No attempt is made to distinguish between the two different isomers which result from additions at either of the double bonds, and in this and the following paper the formulæ for the *mono-adducts* are arbitrary in this respect.

† To avoid other ambiguity and for general simplicity, the polyisoprene adducts are designated throughout this and the following paper as, *e.g.*, phenyl squalene sulphide, it being understood that a hydrogen atom is added together with the thio-radical to give the respective sulphur derivative of a saturated hydrocarbon as shown in the various formulæ.

inertness of rubber seems to represent the extreme of a reactivity trend, cyclohexene > dihydromyrcene > squalene > rubber, of as yet unknown origin.

As regards the activity of the addenda, the order appears qualitatively as, thioglycollic acid > thiophenol ~ isopentaneithiol, which parallels the strength of the related carboxylic acids, malonic, benzoic, and isovaleric. This suggests that the ease of active hydrogen atom and proton removal are similarly conditioned, and that the rupture of the S-H link provides the main contribution to the activation energy and heat of reaction of the addition process.

EXPERIMENTAL

Reactions with Thioglycollic Acid.—(A) cyclohexene (8.2 g.) was shaken with thioglycollic acid (9.2 g.) for 15 mins., a homogeneous solution resulting. After removal of traces of unchanged reactants at 100° in a vacuum, distillation yielded cyclohexylthioglycollic acid (14.5 g.), b. p. 122°/0.1 mm. (Found : C, 55.3; H, 8.1; S, 18.1; equiv., 176. C₈H₁₄O₂S requires C, 55.2; H, 8.05; S, 18.4%; equiv., 174).

To the above acid (5 g.) in chloroform (60 c.c.) were added ice, 3*N*-sulphuric acid (170 c.c.), and then powdered potassium permanganate (8 g.) in small portions with constant shaking. The mixture was then allowed to attain room temperature, decolourised with aqueous sodium bisulphite, the chloroform layer separated, and the aqueous layer extracted with more chloroform. The combined extracts were dried (Na₂SO₄) and concentrated to give the crude solid sulphone, which crystallised from benzene in glistening needles, m. p. 82° (Found : C, 46.4; H, 6.8; S, 15.25; equiv., 200. C₈H₁₄O₄S requires C, 46.6; H, 6.8; S, 15.5%; equiv., 206).

(B) 1-Methylcyclohexene. The olefin (9.6 g.) reacted vigorously with the thio-acid (9.2 g.), the product, isolated by distillation, being 2-methylcyclohexylthioglycollic acid (III), b. p. 135°/0.1 mm. (Found : C, 56.9; H, 8.6; S, 16.6; equiv., 191. C₉H₁₆O₂S requires C, 57.4; H, 8.4; S, 17.0%; equiv., 188).

Oxidation of this sulphide (5 g.) exactly as described for the cyclohexyl homologue gave 4.5 g. of the crude sulphone (IV), which separated from benzene-light petroleum (b. p. 100–120°) as colourless plates, m. p. 96° (Found : C, 48.7; H, 7.3; S, 14.15; equiv., 216. C₉H₁₆O₄S requires C, 49.1; H, 7.3; S, 14.55%; equiv., 220).

Preparation of 1-methylcyclohexylthioglycollic acid (I). (i) 1-Methylcyclohexanol (21 g.) was heated with thioglycollic acid (24 g.) and 2*N*-hydrochloric acid (220 c.c.) for 4 hours at 110°. The cooled mixture was extracted three times with chloroform, the extracts dried (Na₂SO₄), then concentrated to yield a yellow oil (15 g.), which was dissolved in 2*N*-potassium hydroxide, and any unchanged methylcyclohexanol removed by ether extraction. Distillation of the purified oil, regenerated from the alkaline solution by acidification, gave 1-methylcyclohexylthioglycollic acid, b. p. 147°/0.1 mm. (Found : C, 57.5; H, 8.4; S, 16.5%; equiv., 189). (ii) Thioglycollic acid (4.6 g.) was slowly added to a rapidly stirred solution of 1-methylcyclohexene (9.6 g.) in 75% aqueous sulphuric acid (50 g.) cooled to 0°. When addition was complete, the mixture was allowed to warm to room temperature, and stirring continued for a further 15 mins. The product isolated by ether extraction was purified *via* an aqueous alkaline solution as under (i) and then distilled; b. p. 142°/0.1 mm. (Found : C, 57.3; H, 8.6; S, 16.7%; equiv., 193).

The sulphone (II) of the acid (I), prepared in the usual manner and recrystallised from benzene-light petroleum (b. p. 60–80°), had m. p. 85° (Found : C, 49.9; H, 7.4; S, 14.2%; equiv., 218). A mixed m. p. with the 2-methyl isomer (IV) showed a depression of 20–25°.

(C) *Dihydromyrcene.* (a) The olefin (10 g.) (Found : C, 87.05; H, 13.0%; I.V., 364. Calc. for C₁₃H₁₈—₂: C, 86.9; H, 13.1%; I.V., 368) was shaken for 30 mins. with the quantity (6.5 g.) of thio-acid required to saturate one double bond; the resulting homogeneous solution was diluted with benzene (200 c.c.), and unchanged thioglycollic acid removed by several washings with water. Fractionation of the oil obtained from the benzene solution gave: (i) dihydromyrcene, b. p. <140°/14 mm. (1.2 g.); (ii) dihydromyrcene monothioglycollic acid (V), b. p. 170°/0.1 mm. (7.9 g.) (Found : C, 62.55; H, 9.6; S, 13.8; equiv., 234. C₁₂H₂₂O₂S requires C, 62.6; H, 9.6; S, 13.9%; equiv., 230); (iii) high-boiling residue of uncertain composition (5.4 g.). (b) The reaction was repeated but with excess of thioglycollic acid, the product being taken up in benzene and freed from unchanged acid as before. Concentration of the benzene solution gave a viscous oil which, after being kept at 100° in a high vacuum to remove any hydrocarbon, analysed correctly for dihydromyrcene bis(thioglycollic acid) (VI) (Found : C, 52.15; H, 8.0; S, 19.65. C₁₄H₂₆O₄S₂ requires C, 52.25; H, 8.1; S, 19.8%).

Oxidation of the latter acid (VI), carried out in the usual way, yielded a viscous gum which failed to crystallise although analysis showed it to be the desired sulphone (Found : C, 43.2; H, 6.8; S, 16.0. C₁₄H₂₆O₆S₂ requires C, 43.5; H, 6.7; S, 16.6%).

(D) *Squalene.* The hydrocarbon (1 g.) was shaken with the acid (3 g.) and a little ascaridole (0.05 g.) for several weeks at room temperature. The mixture, which remained heterogeneous, was worked up as described for the dihydromyrcene products but gave only unchanged squalene.

(E) *Rubber.* (i) Sol rubber (1 g.) was dissolved in benzene (20 c.c.) containing thioglycollic acid (2 g.) and ascaridole (0.05 g.), and the solution sealed under a vacuum in a "Pyrex" tube 1.5 cm. in diameter. The tube was irradiated for 20 hrs. by a Hanovia S. 500 mercury-vapour lamp placed 6 in. distant. The product, obtained by precipitation with ethyl alcohol followed by extraction (Soxhlet) with alcohol in an atmosphere of nitrogen for 24 hrs., was a white rubber superficially indistinguishable from the starting material (Found : S, 1.7%, which corresponds to 3.8% addition). (ii) A similar reaction mixture to that in (i) was sealed in a vacuum and kept in the laboratory for 2 years; a virtually unchanged rubber resulted (Found : S, 1.1%, *i.e.*, 2.4% addition). (iii) The rubber (1 g.), cut into small pieces, was suspended in thioglycollic acid (10 g.) containing ascaridole (0.05 g.), and the mixture sealed off under a vacuum, and left for 2 years. At the end of this time, the rubber nodules, which showed no sign of change, were removed and well washed with alcohol (Found : S, 0.75%).

Reactions with Thiophenol.—(A) cyclohexene. The olefin (8.2 g.) was dissolved in thiophenol (11

g.), and the solution irradiated with the mercury lamp for 8 hrs. The product, freed from unchanged reactants, was a yellow oil (16 g.) which consisted almost entirely of cyclohexyl phenyl sulphide, b. p. 108°/0.1 mm. (Found: C, 74.95; H, 8.35; S, 16.6. $C_{12}H_{16}S$ requires C, 75.0; H, 8.3; S, 16.65%). Light absorption in cyclohexane showed λ_{max} . 2575 Å. ($\epsilon = 5800$).

Oxidation of the sulphide in the usual way gave the sulphone, which crystallised from methyl alcohol in colourless cubes, m. p. 74° (Found: C, 64.1; H, 7.2; S, 14.1. $C_{12}H_{16}O_2S$ requires C, 64.25; H, 7.1; S, 14.3%).

(B) 1-Methylcyclohexene. Prepared from the hydrocarbon (9.6 g.) and the thiol (11 g.) just as was the cyclohexene derivative, 2-methylcyclohexyl phenyl sulphide (VII) had b. p. 120°/0.1 mm. (Found: C, 75.6; H, 8.75; S, 15.35. $C_{13}H_{18}S$ requires C, 75.6; H, 8.75; S, 15.55%); λ_{max} . 2585 Å. ($\epsilon = 7000$) in cyclohexane.

The sulphone crystallised from methyl alcohol in needles, m. p. 108° (Found: C, 65.5; H, 7.6; S, 13.25. $C_{13}H_{18}O_2S$ requires C, 65.5; H, 7.6; S, 13.45%).

Preparation of 1-methylcyclohexyl phenyl sulphide (VIII). 1-Methylcyclohexene (9.6 g.) was treated with thiophenol (5.5 g.) in the presence of 75% aqueous sulphuric acid (50 g.) as described for the preparation of 1-methylcyclohexylthioglycolic acid, method (ii). The required sulphide was obtained as an oil, b. p. 123°/0.1 mm. (Found: C, 75.6; H, 8.8; S, 15.25%), with λ_{max} . 2680 Å. ($\epsilon = 1500$) in cyclohexane. The corresponding sulphone crystallised from light petroleum (b. p. 80–100°) in needles, m. p. 76° (Found: C, 65.5; H, 7.6; S, 13.3%). A mixed m. p. with the 2-methyl isomer showed a depression of 20–30°.

(C) Dihydromyrcene. Irradiation of a solution of the hydrocarbon (7 g.) in the thiol (10 g.) with the mercury lamp for 8 hrs. yielded an oil (12.2 g.) separable by fractional distillation into phenyl dihydromyrcene sulphide (8 g.), b. p. 135°/0.05 mm. (Found: C, 77.2; H, 9.65; S, 13.1. $C_{16}H_{24}S$ requires C, 77.4; H, 9.7; S, 12.9%), and dihydromyrcene bis(phenyl sulphide) (3.4 g.), a viscous syrup, b. p. 185°/0.05 mm. (Found: C, 73.5; H, 8.25; S, 17.85. $C_{22}H_{30}S_2$ requires C, 73.8; H, 8.4; S, 17.85%).

(D) Squalene. The hydrocarbon (1 g.), thiophenol (2 g.), and ascaridole (0.05 g.) were sealed in a vacuum and irradiated with ultra-violet light for 8 hrs. Removal of unchanged reactants by heating to 100° at 10^{-5} mm. left a mixture evidently consisting of phenyl squalene sulphides (Found: C, 76.6; H, 8.95; S, 13.8. Calc. for 56% addition: C, 77.4; H, 9.0; S, 13.8%).

(E) Rubber. (i) A solution of sol rubber (1 g.), the thiol (2 g.), benzene (20 c.c.), and ascaridole (0.05 g.) was sealed under vacuum in a "Pyrex" tube and irradiated as before for 16 hrs. The product, practically unchanged rubber, had S, 1.45% (i.e., corresponding to 3.25% addition). (ii) A solution of rubber in the thiol (10 g.) without benzene was now employed, and the reaction conditions of (i) repeated. The product had S, 1.8%. (iii) A similar solution to that used in (ii) was sealed in a vacuum and left at room temperature for 2 years. Again, the rubber had undergone little change (Found: S, 1.15%).

Reactions with isoPentanethiol.—(A) cycloHexene. A solution of the olefin (8 g.) in the thiol (8 g.) was irradiated for 8 hrs., the product freed from the starting materials by heating to 100° at 25 mm. pressure, and the residual oil (12 g.) distilled. The exclusive product was cyclohexyl isoamyl sulphide, b. p. 120°/12 mm. (Found: C, 70.9; H, 11.85; S, 17.5. $C_{11}H_{22}S$ requires C, 71.0; H, 11.8; S, 17.2%). The usual oxidation procedure gave the sulphone as an oil which crystallised with some difficulty from ice-cold light petroleum (b. p. 40–60°) as flat leaflets, m. p. 54–56° (Found: C, 59.5; H, 10.0; S, 14.7. $C_{11}H_{22}O_2S$ requires C, 60.5; H, 10.1; S, 14.6%).

(B) 1-Methylcyclohexene. The olefin (10 g.) and thiol (10 g.) were refluxed together for 12 hrs. When freed from excess of reactants, the sole product was a methylcyclohexyl isoamyl sulphide, b. p. 124°/10 mm., which is probably the 2-methyl isomer although this was not formally proved (Found: S, 16.1. $C_{12}H_{24}S$ requires S, 16.0%). By the normal procedure, the sulphone was obtained as an oil, b. p. 149°/0.1 mm. (Found: C, 61.6; H, 10.3; S, 13.5. $C_{12}H_{24}O_2S$ requires C, 62.1; H, 10.35; S, 13.8%).

(C) Dihydromyrcene. The hydrocarbon (10 g.) was dissolved in the thiol (16 g.), and the solution sealed in a vacuum, and left in the laboratory for a year. Fractionation of the product gave: (i) unchanged reactants contaminated with a little sulphide, b. p. <148°/10 mm. (6.2 g.); (ii) isoamyl dihydromyrcene sulphide (Found: C, 73.7; H, 12.3; S, 13.8. $C_{15}H_{20}S$ requires C, 74.4; H, 12.4; S, 13.2%), b. p. 158°/10 mm. (6.3 g.); (iii) material of b. p. <170°/0.05 mm. consisting of a mixture of (ii) and (iv); and (iv) dihydromyrcene bis(isoamyl sulphide) (Found: C, 69.35; H, 12.05; S, 17.9. $C_{20}H_{42}S_2$ requires C, 69.4; H, 12.8; S, 18.5%), b. p. 171–174°/0.05 mm. (12.0 g.).

(D) Squalene. Squalene (1 g.), the thiol (2 g.), and ascaridole (0.05 g.) were sealed together in a vacuum and irradiated for 16 hrs. with the mercury-vapour lamp. The product, freed from unchanged reactants, was a viscous oil (1.8 g.) (Found: S, 16.5. Calc. for 76% addition: S, 16.5%).

(E) Rubber. (i) Sol rubber (1 g.), dissolved in benzene (20 c.c.) containing the thiol (2 g.) and ascaridole (0.1 g.), was sealed in a "Pyrex" tube under a vacuum and irradiated as before for 16 hrs. The solution had then set to a stiff gel, but on trituration with alcohol and drying in a vacuum an insignificantly changed rubber of low sulphur content was obtained (0.9 g.) (Found: S, 0.95%). (ii) A similar solution to that used in (i) was sealed in a vacuum and kept at room temperature for 2 years. Isolated by alcohol precipitation, the rubber was practically unchanged (Found: S, 0.7%).

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