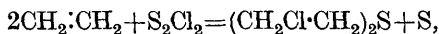


XLVIII.—*The Interaction of Sulphur Monochloride
and Substituted Ethylenes.*

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SINCE it has been shown (Gibson and Pope, T., 1920, **117**, 271) that ethylene is absorbed by sulphur monochloride with production of $\beta\beta'$ -dichlorodiethyl sulphide in accordance with the equation :



it became desirable to ascertain whether a similar reaction occurred with derivatives of ethylene. Sulphur monochloride, purified by distillation with sulphur and absorbent charcoal under 11 mm. pressure, was found not to act upon trichloroethylene on prolonged boiling; on heating the mixture in a sealed tube at 140—150° for some hours a clear, yellow liquid was obtained which soon deposited crystalline sulphur, and on distillation yielded a few drops of an evil-smelling, red oil and a large amount of pentachloroethane boiling at 160°. Sulphur monochloride thus acts merely as a chlorinating agent on trichloroethylene.

The homologues of ethylene, propylene, and β -butylene, were found to act upon sulphur monochloride in precisely the same manner as does ethylene itself; it is thus shown that the equation given above represents a general reaction of the ethylenic hydrocarbons.

EXPERIMENTAL.

$\beta\beta'$ -Dichlorodipropyl Sulphide, $(\text{CHMeCl}\cdot\text{CH}_2)_2\text{S}$.

Sulphur monochloride is introduced into a series of absorption bulbs, which can be vigorously shaken by mechanical means, immersed in a water-bath for the purpose of regulating the temperature. Carefully dried propylene, prepared by the action of *n*-propyl alcohol on phosphoric acid in the manner described by Newth (T., 1901, 79, 915), is then passed through the bulbs at such a speed that some escapes absorption; at temperatures above 30° absorption commences after a short time, and proceeds with increasing speed until a maximum rate is attained. The rate at which propylene is absorbed by sulphur monochloride increases rapidly with rise of temperature; absorption proceeds about twice as fast at 100° as at 60°.

The reaction between propylene and sulphur monochloride is attended by a large evolution of heat which renders necessary very efficient regulation of the temperature; with the apparatus which we employ it is impossible to treat more than 10 grams of sulphur monochloride with propylene at any temperature below 100° without the evolution of torrents of hydrogen chloride and the production of a black, resinous product which gives but a small yield of $\beta\beta'$ -dichlorodi-*n*-propyl sulphide on distillation. The failure of Coffey (this vol., p. 94) to prepare the sulphide by the method now described must be attributed to inefficient temperature control.

When the reaction proceeds below 70° the product is a pale yellow oil from which crystalline sulphur is generally deposited after cooling; when absorption proceeds at 80—100° a dark-coloured oil results, which deposits a large amount of crystalline sulphur on cooling in the absorption bulbs. In either case almost exactly two molecular proportions of propylene are absorbed by each one of sulphur monochloride. It is noteworthy that the catalytic hastening of the absorption of gas by the sulphur monochloride, which Gibson and Pope showed to follow a preliminary addition of $\beta\beta'$ -dichlorodiethyl sulphide, is not observed in the case of propylene; an addition of an already formed reaction product does not influence perceptibly the rate of absorption of propylene.

On distillation under 11 mm. pressure, $\beta\beta'$ -dichlorodipropyl

sulphide, $(\text{CHMeCl}\cdot\text{CH}_2)_2\text{S}$, passes over at $105\text{--}106^\circ$ as a colourless oil, whilst a dark, viscid liquid remains which consists largely of sulphur; the yield of sulphide is about 80 per cent. of that theoretically possible (Found: C = 38.07; H = 6.38; Cl = 38.13; S = 17.24. $\text{C}_6\text{H}_{12}\text{Cl}_2\text{S}$ requires C = 38.50; H = 6.42; Cl = 37.97; S = 17.66 per cent.). Contrary to the statement of Coffey, this substance exerts a considerable vesicant action on the skin; a small drop placed on the forearm caused a painful, red swelling after ten hours and the whole limb became rather painful.

The sulphide is oxidised vigorously by cold nitric acid, and the clear solution deposits an oil on dilution which is probably the sulphoxide; this on heating at 100° with nitric acid is converted into another oily substance, probably the corresponding sulphone, which also refuses to crystallise. On prolonged boiling with 60 per cent. nitric acid the sulphide yields a vapour with the odour of chloropicrin, and when evaporated the residual solution is found to contain sulphuric acid; after treatment with barium carbonate, filtration, and evaporation, a soluble barium salt is obtained which may be purified by crystallisation from water, in which it is very soluble. This compound is *barium* β -chloropropanesulphonate, $(\text{CHMeCl}\cdot\text{CH}_2\cdot\text{SO}_3)_2\text{Ba}\cdot 2\text{H}_2\text{O}$, which crystallises in colourless scales (Found: $\text{H}_2\text{O} = 7.07$. $\text{C}_6\text{H}_{12}\text{O}_6\text{Cl}_2\text{S}_2\text{Ba}\cdot 2\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 7.73$ per cent. Found in anhydrous salt: Ba = 30.57. $\text{C}_6\text{H}_{12}\text{O}_6\text{Cl}_2\text{S}_2\text{Ba}$ requires Ba = 30.37 per cent.).

$\beta\beta'$ -Dichlorodi-sec.-butyl Sulphide,
 $(\text{CHMeCl}\cdot\text{CHMe})_2\text{S}$.

The β -butylene required for the preparation of this compound was made by the action of phosphoric acid on *n*-butyl alcohol as described by King (T., 1919, **115**, 1404), who showed that the product is almost pure β -butylene, $\text{CHMe}\cdot\text{CHMe}$. On passing well-dried β -butylene through sulphur monochloride in the manner already described, absorption proceeds with great rapidity; comparative experiments showed that this hydrocarbon is absorbed about ten times as fast as ethylene by sulphur monochloride at 60° . The speed of absorption increases rapidly as the temperature is raised, and proceeds from four to five times as fast at 100° as at 30° . As with propylene, the addition of preformed reaction product to the sulphur monochloride does not appreciably hasten the absorption of the β -butylene.

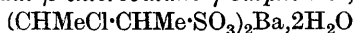
As in the case of propylene absorption, the reaction is attended by a large heat evolution which renders efficient temperature control essential, and the reaction proves uncontrollable when more

than 10 grams of sulphur chloride are treated in our apparatus with β -butylene at 100° ; in this event torrents of hydrogen chloride are evolved, and a black, resinous product results. The most convenient mode of operation consists in starting the absorption at 60° and raising the temperature during one hour to 100° , the gas being passed through at such a rate that some escapes unabsorbed; absorption ceases in about an hour from the commencement. Each molecular proportion of sulphur monochloride absorbs almost exactly two of β -butylene. The product of absorption at 100° is a light brown oil which yields a copious deposit of sulphur on cooling; if the temperature does not rise above 80° during the reaction, a pale yellow oil results, which gives no deposit of sulphur on remaining at the ordinary temperature, although, on heating the oil to 100° and seeding after cooling, some crystalline sulphur is deposited.

When the reaction product is distilled under 11 mm. pressure a pale yellow oil passes over at 120 – 160° and a dark, viscid resin, consisting mainly of sulphur, remains behind; fractional distillation of the oil under reduced pressure yields $\beta\beta'$ -dichlorodi-sec-butyl sulphide as an oil, which has a faint yellow tint and boils at 121 – $122^\circ/11$ mm. The sulphide has a faint odour somewhat recalling that of $\beta\beta'$ -dichlorodiethyl sulphide, and is converted into a white, resinous solid on immersion in liquid air (Found: Cl = 32.85; S = 14.71. $C_8H_{16}Cl_2S$ requires Cl = 33.02; S = 14.89 per cent.). It is almost without vesicant action; a drop left on the back of the hand for eight hours caused no inconvenience, and a little placed under the finger-nail caused only a slight burning sensation after about five hours.

The sulphide is vigorously oxidised by cold nitric acid, but the oil which separates on dilution seems, from analysis, to be a mixture of the corresponding sulphoxide and sulphone; after heating with nitric acid at 100° and evaporating the solution, $\beta\beta'$ -dichlorodi-sec-butylsulphone, $(CHMe \cdot ClCHMe)_2SO_2$, separates as a colourless, viscous oil which becomes converted into a resinous mass on immersion in boiling liquid air (Found: Cl = 27.31. $C_8H_{16}O_2Cl_2S$ requires Cl = 27.74 per cent.).

On prolonged boiling with 60 per cent. nitric acid the sulphide is oxidised with the evolution of vapours having the odour of chloropicrin; the solution contains sulphuric acid, and, after removing this by treatment with barium carbonate, the filtered solution yields the barium salt of a sulphonic acid, which is extremely soluble in water. On recrystallisation from boiling water this salt is obtained in colourless, crystalline scales, and proves to be *barium β -chlorobutane- γ -sulphonate*,



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(Found: $\text{H}_2\text{O} = 7.02$. $\text{C}_8\text{H}_{16}\text{O}_6\text{Cl}_2\text{S}_2\text{Ba}, 2\text{H}_2\text{O}$ requires $\text{H}_2\text{O} = 6.98$ per cent. Found, in anhydrous salt: $\text{Ba} = 28.91$. $\text{C}_8\text{H}_{16}\text{O}_6\text{Cl}_2\text{S}_2\text{Ba}$ requires $\text{Ba} = 28.60$ per cent.).

On boiling the dichlorodi-*sec.*-butyl sulphide for some hours with an alcoholic solution of sodium sulphide and distilling the product in a current of steam, the symmetrical *tetramethyldiethylenedisulphide*, $\text{S} \left\langle \begin{array}{c} \text{CHMe} \cdot \text{CHMe} \\ \text{CHMe} \cdot \text{CHMe} \end{array} \right\rangle \text{S}$, is obtained as a colourless oil with an odour of decaying onions, which boils at $145\text{--}150^\circ/35$ mm. (Found: $\text{S} = 37.71$. $\text{C}_8\text{H}_{16}\text{S}_2$ requires $\text{S} = 36.36$ per cent.).

It is interesting to notice that ethylene, propylene, and β -butylene react in exactly the same manner with sulphur monochloride, yielding β -chloro-substituted alkyl sulphides, together with sulphur, but that the readiness with which reaction occurs is very different in the three cases. A series of determinations of the speed of absorption of these three hydrocarbons by sulphur monochloride has been made under comparable conditions of rate of stirring, etc.; the following table gives the number of litres of gas, measured at N.T.P., absorbed by 135 grams of sulphur monochloride at 60° :

Time in hours.	Volume absorbed.		
	Ethylene.	Propylene.	β -Butylene.
0.4	—	5.5	26.0
0.8	—	23.0	40.2
1.0	0.3	33.0	42.3
1.5	0.6	43.0	43.2
2.0	1.0	43.8	Ended.
3.0	2.7	Ended.	
4.0	6.7		
5.0	23.0		
6.0	43.8		

It is to be concluded from the work now described that the reaction described by Gibson and Pope is a general reaction of ethylene and its homologues.

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