sisted of CCl_3CClF_2 which had the following properties: m. p. 40.5–40.6°; b. p. 91–92°; reported for CCl_3-$CClF_2$[12]: m. p. 40.6°; b. p. 91°. The still residue corresponded to 5% of the original material and was shown to be largely hexachloroethane. Longer reaction times resulted in the formation of larger quantities of this material.

1,2,3-Trichloropentafluoropropane.—The conditions used exactly paralleled those reported above except that a bath temperature of 80–90° was necessary to maintain reflux. For unexplained reasons the recovery was never more than 60% of the starting material.[16] Distillation through an eleven-plate column gave two principal fractions boiling at 70–72° and at 151–152°.

The low-boiling fraction which constituted 70% of the recovered material after redistillation had the following properties: m. p. −5°; b. p. 71–72°; n^{25}_D 1.3490. An authentic sample of $CClF_2CCl_2CF_3$[17] had the following properties: m. p. −4.3°; n^{25}_D 1.3490. A mixture of the two samples melted −4 to −5°.

The high b. p. material which composed 20% of the recovered material had the following properties after redistillation and crystallization from alcohol: m. p. 108.9–109.2°, b. p. 151.8–152.0°; reported for $CCl_3CCl_2CF_3$ m. p. 109.0°, b. p. 153.1°. No other $C_3Cl_5F_3$ compound melts near $CCl_3CCl_2CF_3$.[17]

Acknowledgment.—We are indebted to Dr. J. R. Dunning and members of the Columbia University cyclotron group for the preparation of radioactive chlorine and to Drs. J. Bigeleisen and A. Kirschenbaum for counting analytical samples.

Summary

Aluminum chloride has been found to cause rearrangement as well as replacement of fluorine by chlorine, when reacting with some saturated chlorofluorocarbons. The rearrangement reaction was shown to proceed by an intramolecular mechanism and to lead to the formation of compounds containing two or three fluorines on one carbon.

ITHACA, NEW YORK RECEIVED[18] AUGUST 4, 1949

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[16] The possible formation of volatile cleavage products corresponding to a reversed Prins type reaction was not investigated.

[17] Henne and Whaley, THIS JOURNAL, **64**, 1157 (1942).

[18] This paper was originally submitted February 4, 1949.

[CONTRIBUTION FROM THE DEPARTAMENTO DE QUÍMICA DA FACULDADE DE FILOSOFIA, CIÊNCIAS E LETRAS DA UNIVERSIDADE DE SÃO PAULO, BRASIL]

The Action of Raney Nickel upon Sulfur Compounds. II. Mercaptals, Mercaptols and Disulfides[1,2]

BY H. HAUPTMANN AND B. WLADISLAW

Recently we reported briefly upon two different types of reactions observed when Raney nickel is allowed to act upon aromatic mercaptals and mercaptols. During these experiments the Raney nickel had to be freed from the hydrogen adsorbed in the course of its preparation by heating *in vacuo* and the reaction had to be carried out in the absence of hydrogen donating solvents. When aromatic mercaptals and mercaptols were refluxed in xylene solution in the presence of Raney nickel previously heated at 100°, binuclear hydrocarbons were formed. Thus, from formaldehyde diphenylmercaptal (I) we were able to isolate diphenyl in a yield of 9%. This transformation is analogous to the conversion of diphenyl sulfide into diphenyl[1]. It has been discussed[3] as a possible side reaction in hydrogenolytic desulfurization and called a "Wurtz type reaction," but previously it had not been observed by any investigator.

From mercaptals of benzaldehyde (II, III) or mercaptols of acetophenone (IV), stilbene or its substitution products were obtained in yields up to 37%. The formation of stilbene under these conditions is not entirely unexpected in view of the report by Campaigne, *et al.*,[4] who isolated *trans*-dimethylstilbene (18% yield) after treating trithioacetophenone with Raney nickel in xylene solution and those of Bergmann, *et al.*,[5] who obtained 1,2-di-(9-phenanthryl)-ethylene from polymeric phenanthryl-9-thioaldehyde.[6]

Campaigne, *et al.*, supposed that their low yield was due to hydrogenolytic formation of volatile ethylbenzene, and this is quite probable since they made no attempt to remove the adsorbed hydrogen from the Raney nickel. We, too, considered hydrogenolytic desulfurization to benzene and toluene to be the cause of our relatively low yields of diphenyl and stilbene. Therefore, we heated the Raney nickel *in vacuo* at 200° which resulted in the evolution of a considerable amount of hydrogen. In the following, this will be recognized as "hydrogen-free Raney nickel" in contrast to the "hydrogen-poor Raney nickel" previously heated at only 100°. With hydrogen-free Raney nickel the yield of stilbene was im-

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[1] Paper I of this series, H. Hauptmann, B. Wladislaw and P. F. Camargo, *Experientia*, **4**, 385 (1948).

[2] This paper is extracted from a thesis presented to the Faculdade de Filosofia, Ciências e Letras da Universidade de São Paulo by B. Wladislaw in partial fulfillment of the requirements for the degree of "Dr. em Ciencias."

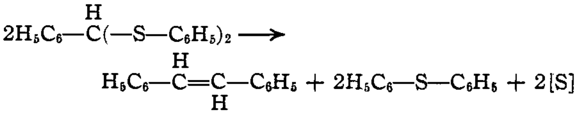
[3] R. Mozingo, D. E. Wolf, S. A. Harris and K. Folkers, THIS JOURNAL, **65**, 1013 (1943).

[4] J. K. Cline, E. Campaigne and J. W. Spies, *ibid.*, **66**, 1136 (1944).

[5] F. Bergmann and S. Israelashwili, *ibid.*, **67**, 1951 (1945).

[6] Stilbenes are the main reaction products when polymeric thioaldehydes or thioketones are heated with copper bronze. See J. H. Wood, J. A. Bacon, A. W. Meibohm, W. H. Throckmorton and G. P. Turner, *ibid.*, **63**, 1334 (1941); R. C. Fuson and C. E. Best, *ibid.*, **67**, 155 (1945); L. Gattermann, *Ber.*, **28**, 2869 (1895), and **29**, 2944 (1896). Detailed bibliographic survey by E. Campaigne, *Chem. Revs.*, **39**, 1 (1946).

proved (up to 69%) but no diphenyl was formed. Instead, diphenyl sulfide was obtained in a yield of 88% as represented by the equation



$$2H_5C_6{-}\overset{H}{C}({-}S{-}C_6H_5)_2 \longrightarrow H_5C_6{-}\overset{H}{C}{=}\underset{H}{C}{-}C_6H_5 + 2H_5C_6{-}S{-}C_6H_5 + 2[S]$$

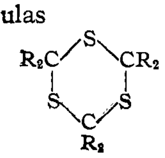
This seemed to be a possible route to the synthesis of aromatic thioethers of the type Ar–S–Ar, especially since the formation of stilbene or other non-volatile by-products could be avoided by employing simple aliphatic aldehydes or ketones instead of benzaldehyde. In order to test this hypothesis, various simple aromatic thioethers were prepared by refluxing formaldehyde mercaptals in xylene solution in the presence of hydrogen-free Raney nickel. Thus, diphenyl sulfide was formed from formaldehyde diphenylmercaptal in a yield of 71%, di-*p*-tolyl sulfide from formaldehyde di-*p*-tolylmercaptal (V) in a yield of 71% and di-*β*-naphthyl sulfide from formaldehyde-di-*β*-naphthylmercaptal (VI) in a yield of 68%. It is apparent that this reaction is not limited to the mercaptals of formaldehyde and a current study is under way using other mercaptals and mercaptols in order to find out whether higher yields may be obtained by their use.

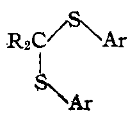
The formation of thioethers, however, was observed under these conditions only when mercaptals are used in which the sulfur was connected directly to an aromatic ring. When benzaldehyde dibenzylmercaptal (VII) was refluxed in xylene solution in the presence of hydrogen-free Raney nickel, all the sulfur was bound on the Raney nickel, and in our hands only stilbene and 1,2-diphenylethane could be isolated from the sulfur-free reaction mixture.

It is obvious that the behavior of other types of sulfur compounds in the presence of Raney nickel should be studied. Disulfides, for example, should react in a similar manner to that of the mercaptals, forming thioethers in the presence of hydrogen-free nickel. This could be demonstrated: diphenyl disulfide (VIII) was transformed into diphenyl sulfide in a yield of 82%.

Our reaction products were compared with authentic samples when possible, and frequently characteristic derivatives were prepared. Thus, all sulfides were oxidized to the easily identified crystalline sulfones.

Mercaptols and mercaptals behave like the above-mentioned thioaldehydes and thioketones[5,6] in regard to the formation of stilbene. The reason for this behavior seems to be that both groups of compounds possess two sulfur atoms connected to the same carbon atom as illustrated by the formulas





We consider the formation of binuclear hydrocarbons, as well as that of sulfides, to be a surface-catalyzed reaction with intermediate formation of radicals. Two types of radicals are formed: (1) benzylidene radicals which recombine forming stilbene, and (2) arylmercapto radicals. If these radicals form intermediate compounds of the type $Ni(SR)_2$ as Bougault, *et al.*,[7] propose for the hydrogenolytic desulfurization or if they are held on the metal surface by adsorption forces is an open question. We could never observe any evidence for the formation of such compounds and, moreover, it seems that they would exist only on the nickel surface since they would hardly be soluble. If this agreed, there is almost no difference between the two viewpoints.

What happens to these radicals depends on the quantity of hydrogen still present on the metal surface. If its concentration is low, as in the hydrogen-free nickel, sulfides are formed. If it is high enough, as in the hydrogen-poor nickel, hydrogenolytic desulfurization occurs and the aryl radicals are either hydrogenated to the corresponding hydrocarbons or, if there is insufficient hydrogen, recombine forming biaryls.

A very interesting analogy to the phenomena which we observed is found in the formation of diphenyl in addition to benzene when bromobenzene is heated in methanol in the presence of palladium on calcium carbonate and of alkali. Mayo and Hurwitz[8] who studied this reaction recently also consider it as being a surface-catalyzed reaction and assume that the diphenyl comes from combination of aryl radicals. As was observed in our own work the yield of diphenyl is reduced and that of benzene is increased by the presence of hydrogen.

The observation that Raney nickel transforms sulfur compounds into diaryls but has little

TABLE I

Number	Compound	M. p. or b. p., °C.	Yield, %
I	Formaldehyde diphenylmercaptal[a]	M. p. 40	88.7
II	Benzaldehyde diethylmercaptal[b]	B. p. 24 mm., 150	80
III	Benzaldehyde diphenylmercaptal[c]	M. p. 52	90
IV	Acetophenone ethylenemercaptol	B. p. 11 mm., 162–163.5	78.8
V	Formaldehyde di-*p*-tolylmercaptal[d]	M. p. 29–30	73.9
VI	Formaldehyde di-*β*-naphthylmercaptal	M. p. 103–104	80.4
VII	Benzaldehyde dibenzylmercaptal[e]	M. p. 55–60	74.4

[a] W. H. Taylor, THIS JOURNAL, **57**, 1065 (1935). [b] E. Baumann, *Ber.*, 18, 885 (1885). [c] The yield of 90% was obtained by adding a few drops of concentrated hydrochloric acid to the solution of the reactants in glacial acetic acid. When proceeding according to the indication of Taylor[a] the yield was 73.9%. [d] E. Fromm, A. Forster and B. Scherschewitzi, *Ann.*, **394**, 343 (1912), the compound is described as being an uncrystallizable oil. [e] E. Fromm and E. Junnius, *Ber.*, **28**, 1111 (1895); E. Fromm and F. Erfurt, *ibid.*, **42**, 3811 (1909).

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[7] T. J. Bougault, E. Cattelain and P. Chabrier, *Bull. soc. chim.*, **208**, 657 (1933).

[8] F. R. Mayo and M. D. Hurwitz, THIS JOURNAL, **71**, 776 (1949). See this paper for previous literature.

TABLE II

Comp.	Ni Heated at, °C.	Re-fluxed, hr.	Compound obtained	M. p. or b. p., °C.	Yield, %	Characterized as	M. p., °C.	Yield, %
I	100	44^a	Diphenyl	M. p. 69–70^b	9.2	*p,p'*-Dibromodiphenyl	164^b	83.3
	200	17.5	Diphenyl sulfide	B. p. 136–137, 7 mm.	71.4	Diphenylsulfone	125–126^b	91
II	100	7^a	Stilbene	M. p. 123–124^b	35.5	....	......	..
	200	14.5^a	Stilbene	M. p. 123–124^b	69	....	......	..
III	200	17.5	Stilbene and diphenyl	M. p. 123–124^b	60	....	......	..
			sulfide	B. p. 157–159, 20 mm.	88	Diphenylsulfone	122–124^b	75
IV	200	16	*trans*-Dimethylstilbene	M. p. 105–107	30^c	Dibromodiphenylethane	152–153	84.7
V	200	15	Di-*p*-tolyl sulfide	M. p. 56–57^b	71.1	Di-*p*-tolylsulfone	159^b	93.1
VI	200	12.5	Di-β-naphthyl sulfide	M. p. 150–151^b	68.7	Di-β-naphthylsulfone	176–177	95
VII	100	5^a	Stilbene	M. p. 123–124^b	37.4	....	......	..
	200	20^a	Stilbene and diphenyl-	M. p. 123–124^b	^{d}	....	......	..
			ethane	M. p. 51–52^b		....	......	..
VIII	200	15	Diphenyl sulfide	B. p. 127–128	82.1	Diphenylsulfone	123–124^b	87

[a] After this time the solution was sulfur-free. [b] Mixed melting points with authentic material were taken and no depression was observed. [c] There remained a resinous residue which could not be crystallized nor fractionated. [d] From 10 g. of benzaldehyde dibenzylmercaptal 6 g. of a mixture of both substances was obtained. The quantitative separation was impossible.

effect upon bromobenzene seems to indicate that differences in specific affinities between the hetero atom and the metal are of great importance in these reactions. Nickel is well known for being a typical calcophilic element.

Experimental[9]

1. **Preparation of the Mercaptols and the Mercaptals.**—Table I indicates the methods of preparation and physical properties of the mercaptals and mercaptols employed.

Acetophenone Ethylenemercaptol (IV).—It was prepared by passing a stream of hydrogen chloride through the chilled mixture of 14.8 g. (0.12 mole) of acetophenone, 12 g. of 1,2-ethanedithiol and 4 cc. of glacial acetic acid. After removing unaltered 1,2-ethanedithiol and hydrogen chloride *in vacuo* the reaction mixture was extracted with ether. The residue of the dried ethereal solution was fractionated. The mercaptol distilled at 162–163.5° (11 mm.); yield, 19 g. or 78.8%.

Anal. Calcd. for $C_{10}H_{12}S_2$: S, 32.65. Found: S, 32.74.

Formaldehyde Di-β-naphthylenemercaptal (VI).—Prepared in an analogous manner from 2 g. (0.012 mole) of β-thionaphthol, 400 mg. of formalin 40% (180 mg. formaldehyde, 0.06 mole) and 2 cc. of glacial acetic acid; recrystallized from alcohol; m. p. 103–104°; yield, 1.6 g. or 80.4%.

Anal. Calcd. for $C_{21}H_{16}S_2$: S, 19.28. Found: S, 19.55.

Preparation of Raney Nickel.—After being prepared following the usual procedure[10] the nickel was thoroughly washed with alcohol and with benzene. Then it was transferred to a round-bottom flask equipped with a side-arm and a dropping funnel. Benzene was evaporated *in vacuo* in a water-bath and the heating continued for two hours at the desired temperature of 100 or 200°. The Raney nickel then was allowed to cool *in vacuo* and enough dry xylene was added through the dropping funnel to cover it completely so that direct contact with air was avoided. The nickel was not stored but was used immediately.

Reaction of the Mercaptals with Raney Nickel.—General procedure: the mercaptals dissolved in xylene were added to a xylene suspension of Raney nickel. The proportion was about five parts in weight of Raney nickel to one part of mercaptal. The suspension was stirred vigorously and boiled under reflux[11] for the time indicated in Table II. The Raney nickel was then filtered and thoroughly washed with xylene. The xylene was evaporated *in vacuo* and the residual reaction products separated either by distillation or crystallization, or both, according to the physical properties of the product obtained. The reaction products were then purified, identified and, if possible, transformed into characteristic derivatives.

Acknowledgment.—We wish to express our thanks to the Rockefeller Foundation for a grant supporting this work and to Dr. E. Giesbrecht and Dr. W. Safiotti for some authentic materials which they supplied for comparison.

Summary

1. Aromatic mercaptals, mercaptols and disulfides are transformed into simple thioethers by action of Raney nickel that has been freed from hydrogen by heating *in vacuo* at 200°.

2. When hydrogen is not completely removed, binuclear hydrocarbons such as diphenyl or dibenzyl are formed.

3. When benzaldehyde mercaptals or acetophenone mercaptols are employed, stilbene or its substitution products are obtained in addition to the compounds cited above.

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[9] All melting points were measured with a Kofler melting point apparatus and the sulfur analyzed using the method of A. Schoeberl, R. Jaczinsky and P. Rambacher, *Z. angew. Chem.*, **50**, 334 (1937).

[10] *E. g.*, Covert and H. Adkins, THIS JOURNAL, **54**, 4116 (1932); P. Ruggli and E. Preiswerk, *Helv. Chim. Acta*, **22**, 495 (1939).

[11] In some experiments a stream of nitrogen was passed through the solution to avoid the access of oxygen, but no difference between those runs and those not protected against oxygen could be observed.