#### [Contribution from the Departamento de Quimica da Faculdade de Filosofia, Ciencias e Letras da Universidade de Sao Paulo, Brasil]

# The Action of Raney Nickel on Sulfur Compounds. III.<sup>1</sup> Aromatic Thioesters<sup>2</sup>

## BY H. HAUPTMANN AND B. WLADISLAW

When our studies concerning the action of Raney nickel on several types of sulfur compounds were extended to thioesters it was found<sup>3</sup> that the results depended upon the previous treatment of the Raney nickel in a manner similar to that observed for the mercaptals and mercaptols.<sup>1</sup> When the metal was heated at  $100^{\circ}$  and, therefore, only incompletely freed from the adsorbed hydrogen, sulfur-free reaction compounds were formed, but with an almost completely hydrogenfree nickel obtained by heating the metal at  $200^{\circ}$ sulfides were the reaction products.

When phenyl thiobenzoate is refluxed in xylene solution in the presence of the "hydrogen-free Raney nickel,"<sup>1</sup> diphenyl sulfide is formed. From 10 g. of thiobenzoate we obtained 5.9 g. of diphenyl sulfide. This high yield suggested that both phenyl radicals of the molecule take part in the diphenyl sulfide formation. Therefore, when we submitted  $\alpha$ - and  $\beta$ -naphthyl thiobenzoate to the same reaction the mixed thioethers were obtained: phenyl  $\alpha$ -naphthyl sulfide in a yield of 52% and phenyl  $\beta$ -naphthyl sulfide in a yield of 42%. In both cases the two possible simple thioethers, diphenyl sulfide and  $\alpha$ - or  $\beta$ -dinaphthyl sulfide, were also formed.

These results show that the carbonyl group has been split off and that carbon monoxide should be produced during the reaction. This was established by heating  $\alpha$ -naphthyl thiobenzoate and "hydrogen-free Raney nickel" to 140° in a stream of nitrogen. Carbon monoxide produced in this manner readily reduced palladium chloride to metallic palladium.

By these observations it was proven that the decomposition of aryl thiobenzoates in the presence of "hydrogen-free Raney nickel" follows the scheme

$$H_{\delta}C_{6}-C-S-Ar \longrightarrow H_{\delta}C_{6}-S-Ar + CO$$

The yields of mixed thioethers so obtained make the new reaction an interesting method for the preparation of this class of compounds, and work is in progress to determine the relationship between substitution in the aromatic nucleus and yields of products.

When benzyl thiobenzoate was employed we (1) H. Hauptmann and B. Wladislaw, THIS JOURNAL, 72, 707

(1950).
(2) This paper is extracted from a thesis presented to the Faculdade de Filosofia, Ciencias e Letras de Universidade de Sao Paulo by B. Wladislaw in partial fulfillment of the requirements for obtaining the degree of "Dr. em Ciencias."

(3) H. Hauptmann, B. Wladislaw and P. F. Camargo, Experientia, 4, 385 (1948).

obtained phenyl benzyl sulfide and diphenyl sulfide as expected, but instead of dibenzyl sulfide, 1,2-diphenylethane was formed. This is analogous to the behavior of benzaldehyde dibenzylmercaptal under identical conditions<sup>1</sup> and confirms the idea that the sulfur is less firmly bound to the benzyl radical than to the aromatic nucleus.

Furthermore, we studied the behavior of a few thioesters in the presence of Raney nickel previously heated at 100°. From phenyl thioacetate, diphenyl was obtained in 29% yield; about the same yield of diphenyl (28%) was obtained from ethyl thiobenzoate. This result shows beyond doubt that diphenyl may also be formed from the benzene nucleus directly attached to the >CO group which is eliminated during the reaction. When phenyl thiobenzoate was treated with "hydrogen-poor Raney nickel" in the same manner, the yield of diphenyl was 46% almost twice as much as obtained with the compounds that have only one benzene ring. No other reaction products could be isolated. Thus, we conclude that hydrogenolytic desulfurization occurred in considerable amount.

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

For the interpretation of our observations it seemed important to make sure that common esters are stable under the conditions of the reaction. Therefore, phenyl benzoate was heated with Raney nickel under identical conditions and was recovered unchanged. This observation emphasizes the importance of the sulfur as the key atom of the whole reaction. We believe that it is responsible for the first step of the reaction, that is, the adsorption of the organic compound on the metallic surface. It is well known that considerable attraction comparable to the forces of co-valency is developed in these chemisorptions.<sup>4</sup> During the adsorption process the bond between the sulfur and the benzoyl group is weakened and finally broken, so that a free benzoyl radical is produced.

There are several examples in which acyl radicals may split off carbon monoxide during its stabilization reactions. Thus, when benzoyl chloride is treated with nickel and hydrochloric acid, diphenyl, among other reaction products,<sup>5</sup> is formed. Valeryl chloride is transformed by

(4) See c. g. W. A. Waters, "The Chemistry of Free Radicals," Oxford University Press, 1946, p. 218.

(5) A. Mailhe and P. Godon, Bull. soc. chim., 19, 449 (1916); Chem. Zentr., 88, 1456 (1917). TABLE I

		heated	d Re- fluxed,		B. p. or m	. p.				Yield
	Ester	°C.	hr.	Compound obtained	°C.	Мm.	. Yield	Characterized as	М.р.	%
I	Phenyl thiobenzoate <sup>a</sup>	200	16.5	Diphenyl sulfide	126 - 126.5	3	71%	Diphenylsulfone <sup>b</sup>	123 - 124	80.7
		100	10	Diphenyl	м 70 <sup>b</sup>		46.2	4,4'-Dibromodipheny1 <sup>b</sup>	164	75
<b>I</b> 1	α-Naphthyl benzoate <sup>c</sup>	200	15	Diphenyl sulfide <sup>d</sup>	135-137	7	<22.9>	Diphenylsulfone <sup>b</sup>	125 - 126	88.9
				Phenyl α-naphthyl sulfide	M 40-41.5		52.5	Phenyl-α-naphthyl- sulfone	99–100	94.2
				Di-α-naphthyl sulfide <sup>4</sup>	М 109-110		<19.5>	Di-a-naphthylsulfone	186-187	95.4
111	β-Naphthyl benzoate <sup>6</sup>	200	6	Diphenyl sulfide <sup>d</sup>	125 - 126		<20>	Diphenylsulfone <sup>b</sup>	125 - 126	86
	-			Phenyl $\beta$ -na <b>ph</b> thyl sulfide	M 50-51		42	Phenyl-β-naphthyl- sulfone	115-116	95
				Di-β-naphthyl sulfide <sup>d</sup>	M 150-151		<39.1>	$Di-\beta$ -naphthylsulfone	176.5-177	91.7
IV	Benzyl thiobenzoate <sup>f</sup>	200	15.5	Diphenyl sulfide	165	15	?	Diphenylsulfone <sup>b</sup>	125 - 126	75.2
				Benzphenyl sulfide <sup>b</sup>	M 40-41		45	Benzylphenylsulfone <sup>b</sup>	147.5 - 149	92
				Diphenylethane <sup>b,d</sup>	M 51-52		<8.4>		· · · · · · · ·	
V	Phenyl thioacetate <sup>g</sup>	100	60	Dipheny1 <sup>b</sup>	M 69-70		29.3	4,4'-Dibromodiphenyl <sup>b</sup>	165	80
Vt	Ethyl thiobenzoate <sup>a, h</sup>	100	20	Diphenyl <sup>b</sup>	M 69-70		28.3	4,4'-Dibromodiphenyl <sup>b</sup>	164	80

<sup>a</sup> R. Schiller and R. Otto, *Ber.*, 9, 1635 (1876). <sup>b</sup> Mixed melting point with authentic material was taken and odepression observed. <sup>c</sup> After this time the solution was sulfur-free. <sup>d</sup> The yields were calculated considering the formation of simple thioethers as being an independent side reaction. <sup>e</sup> F. Krafft and R. Schönherr, *Ber.*, 22, 825 (1889). <sup>f</sup> R. Otto and R. Hiden, *Ber.*, 13, 1285 (1880). <sup>e</sup> H. W. Hickler, *Ber.*, 7, 1312 (1874). <sup>h</sup> Pratt and Reid, THIS JOURNAL, 57, 37 (1937).

nickel into carbon monoxide and isobutylene,<sup>6</sup> and finally the formation of carbon monoxide has been observed in a series of photochemical reactions in which acylradicals appear as intermediates.<sup>7</sup>

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There remain phenyl and arylmercapto radicals after splitting off the >CO group. When almost no hydrogen is present on the metal surface, these form the mixed sulfides. In the presence of "hydrogen-poor Raney nickel," two reactions occur: formation of simple aromatic hydrocarbons as benzene and, when the hydrogen is used up, formation of binuclear hydrocarbons as diphenyl. This scheme does not explain the formation of simple thioethers, and it is possible that these compounds could come from secondary disproportion of the mixed thioethers. We observed the formation of diphenyl sulfide and 1,2diphenylethane from phenylbenzyl sulfide in the presence of "hydrogen-free Raney nickel" which seems to support this idea. The special behavior of the benzyl radical,1 however, makes it desirable now to try this reaction with purely aromatic thioethers.

#### Experimental

The melting points were measured with a Kofler melting point apparatus; the sulfur analyzed using the method of Schoeberl.<sup>8</sup> The Raney nickel was prepared as described in our previous paper.<sup>1</sup> Three representative experiments are presented below. The results are assembled in Table 1.

Reaction of  $\alpha$ -Naphthyl Thiobenzoate with "Hydrogen-free" Raney Nickel.—A solution of 13.7 g. of  $\alpha$ naphthyl thiobenzoate in about 50 ml. of xylene was added to approximately 70 g. of Raney nickel heated previously *in vacuo* at 200° for two hours and the mixture refluxed for fifteen hours with continuous agitation. Then the nickel was filtered off and thoroughly washed with xylene. From the combined xylene solutions the solvent was removed under reduced pressure and the liquid residue distilled *in* 

(7) W. A. Waters, "The Chemistry of Free Radicals," Oxford University Press, 1946, p. 116.

(8) A. Schoeberl, R. Jaczinsky and P. Rambacher, Z. angew. Chem., 50, 334 (1937).

vacuo. Two fractions, containing sulfur, were obtained, the first with a b. p.  $135-137^{\circ}$  (7 mm.), yield 1.1 g. or 22.9%; the second with a b. p.  $175-185^{\circ}$  (0.1 mm.); and a residue that solidified on cooling and after recrystallization from ethanol melted at  $109-110^{\circ}$  (di- $\alpha$ -naphthyl sulfide, m. p.  $110^{\circ}$ )<sup>9</sup>; yield, 1.45 g. or 19.5%. The second fraction was redistilled at 0.1 mm. and the fraction boiling between  $175-177^{\circ}$  dissolved in ethanol and cooled in the ice box. A crystalline substance precipitated after several days. It was recrystallized once more from ethanol; m. p.  $41-41.5^{\circ}$  (phenyl  $\alpha$ -naphthyl sulfide  $41.8^{\circ}$ ),<sup>10</sup> yield, 6.4 g. or 52.5%. The three sulfides were oxidized with hydrogen peroxide in glacial acetic acid. The yields and melting points of the sulfones are shown in Table I. **Reaction of Phenyl Thiobenzoate with ''Hydrogen-poor Raney Nickel.''**-A xylene solution of 15 g. of phenyl thiobenzoet was added to a xylene suspension of about  $45 \, g$ , of

Reaction of Phenyl Thiobenzoate with "Hydrogen-poor Raney Nickel."—A xylene solution of 15 g. of phenyl thiobenzoate was added to a xylene suspension of about 45 g. of Raney nickel previously heated at  $100^{\circ}$  in vacuo for two hours and the mixture refluxed in the presence of nitrogen. After five hours, a filtered sample of the solution was dried and the residue examined for the presence of sulfur. Since the reaction was positive, about 30 g. more Raney nickel was added and the refluxing continued for five hours. After this time no sulfur could be found in the solution. The Raney nickel was then removed by filtration and thoroughly washed with xylene. From the combined filtrates, the xylene was removed and the oily residue fractionated at atmospheric pressure. The fraction distilled between 250 and 252° solidified and was recrystallized from ethanol; m. p. 70°, mixed m. p. with diphenyl (Merck) 69-70°, yield, 5 g. or 46.2%. The substance was brominated and the compound obtained melted at 164°; mixed m. p. with 4,4'-dibromodiphenyl, 164°, yield 75%.

Reaction of Benzyl Thiobenzoate with "Hydrogenfree Raney Nickel."—A xylene solution of 15 g. of benzyl thiobenzoate was added to about 75 g. of Raney nickel previously heated at  $200^{\circ}$  in vacuo for two hours, the nixture refluxed for fifteen and one-half hours in a stream of nitrogen. The catalyst was filtered, the solvent removed and distilled in vacuo in the described manner. At 12 mm. a large fraction boiled between 162-215°. Further distillations gave no additional products, but by treatment of the residue with ethanol a crystalline substance could be obtained which, after two recrystallisations, melted at  $40-41^{\circ}$  (mixed m. p. with phenyl benzyl sulfide  $40-41^{\circ}$ , sulfone m. p. 147.5-149°, mixed m. p. with phenyl benzyl sulfone 147.5-149°), yield, 5.9 g. or 45%. The alcoholic mother liquor was fractionated, and 2.91 g. of a sulfurcontaining liquid (b. p.  $160-169^{\circ}$  (12 mm.)) was ob-

(9) F. Krafft and R. Schoenherr, Ber., 22, 825 (1889).
(10) E. Bourgeois, *ibid.*, 28, 2318 (1895).

<sup>(6)</sup> A. Mailhe, Compt. rend., 180, 1111 (1925).

tained. No separation of pure substances was possible. Therefore, 0.8 g. of the residue was treated with hydrogen peroxide in glacial acetic acid and 0.7 g. of diphenylsulfone isolated.

In order to prove the eventual presence of 1,2-diphenylethane in a qualitative manner, 1.8 g. of the sulfur-con-taining oil and 1.3 g. of dimethyl sulfate were heated on the water-bath. After one hour the mixture was poured into water and extracted with ether. The evaporation of the dried ethereal solution led to an oily residue which deposited crystals from ethanol. After two recrystallizations from ethanol these crystals melted at  $51-52^{\circ}$  (mixed m. p. with 1,2-diphenylethane 51-52°); yield 300 mg.

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## Summary

1. Mixed thioethers are the main reaction products when thiobenzoic esters are refluxed in xylene solution in the presence of Raney nickel freed from hydrogen by previous heating at 200° in vacuo.

2. When hydrogen has not been completely removed, binuclear hydrocarbons such as diphenyl are formed.

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#### N-Methyl-10-phenyldecahydroisoquinoline The Angular Aryl Group. II.

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In a previous publication<sup>2</sup> it was pointed out that the Gulland and Robinson formula for morphine may be regarded as a substituted octahydroisoquinoline having an angular aryl group.<sup>3</sup> This portion of the morphine skeleton is

shown by solid lines in formula I. Although



much work has been done on the synthesis of morphine analogs, the portion of the molecule outlined in I has not previously been synthesized and tested for analgesic activity.<sup>4</sup> The synthesis of N-methyl-10-phenyldecahydroisoquinoline has now been accomplished and the reaction scheme for its synthesis is outlined below.

The conversion of II to III was effected in 64% yield by addition of hydrogen cyanide followed by dehydration. The procedure for this was evolved using 2-phenylcyclohexanone as a model. An attempt was made to prepare the corresponding acid of III as a derivative, but hydrolysis did not occur readily and with 48% hydrobromic acid the correspond-ing lactone (IV) was formed.

Hydrogenation of III gave V in good yield.

(1) (a) Sherman Clarke Fellow, 1948-1949; (b) present address: University of Illinois, Urbana, Illinois

(2) Boekelheide, THIS JOURNAL, 69, 790 (1947).

(3) Gulland and Robinson, Mem. Proc. Manchester Lit. & Phil. Soc., 69, 79 (1925).

(4) Bergel and Morrison, Quart. Rev., 2, 349 (1948).

Cleavage of the ether linkage was accomplished with hydrobromic acid, and the crude bromoamine (VI) was cyclized directly to VIII. The cyclization product was impure and attempted



purification resulted in the isolation of a product having the correct composition for VII. Since it was found that IX could be readily purified, the cyclization product, which consisted predominantly of VIII, was subjected directly to reductive alkylation. It was of interest that the picrate of IX was homogeneous, indicating that only one of the possible forms, presumably the