

TABLE I

Ester	Ni heated		Compound obtained	B. p. or m. p.		Yield	Characterized as	M. p.	Yield %
	at °C.	Re-fluxed, hr.		°C.	Mm.				
I Phenyl thiobenzoate ^a	200	16.5	Diphenyl sulfide	126-126.5	3	71%	Diphenylsulfone ^b	123-124	80.7
	100	10	Diphenyl	M 70 ^b		46.2	4,4'-Dibromodiphenyl ^b	164	75
II α -Naphthyl benzoate ^c	200	15	Diphenyl sulfide ^d	135-137	7	<22.9>	Diphenylsulfone ^b	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 ^d	M 109-110		<19.5>	Di- α -naphthylsulfone	186-187	95.4
III β -Naphthyl benzoate ^e	200	6	Diphenyl sulfide ^d	125-126		<20>	Diphenylsulfone ^b	125-126	86
			Phenyl β -naphthyl sulfide	M 50-51		42	Phenyl- β -naphthyl-sulfone	115-116	95
			Di- β -naphthyl sulfide ^d	M 150-151		<39.1>	Di- β -naphthylsulfone	176.5-177	91.7
IV Benzyl thiobenzoate ^f	200	15.5	Diphenyl sulfide	165	15	?	Diphenylsulfone ^b	125-126	75.2
			Benzophenyl sulfide ^b	M 40-41		45	Benzylphenylsulfone ^b	147.5-149	92
			Diphenylethane ^{b,d}	M 51-52		<8.4>
V Phenyl thioacetate ^g	100	60	Diphenyl ^b	M 69-70		29.3	4,4'-Dibromodiphenyl ^b	165	80
VI Ethyl thiobenzoate ^{a,h}	100	20	Diphenyl ^b	M 69-70		28.3	4,4'-Dibromodiphenyl ^b	164	80

^a R. Schiller and R. Otto, *Ber.*, **9**, 1635 (1876). ^b Mixed melting point with authentic material was taken and no depression observed. ^c After this time the solution was sulfur-free. ^d The yields were calculated considering the formation of simple thioethers as being an independent side reaction. ^e F. Krafft and R. Schönherr, *Ber.*, **22**, 825 (1889). ^f R. Otto and R. Hiden, *Ber.*, **13**, 1285 (1880). ^g H. W. Hickler, *Ber.*, **7**, 1312 (1874). ^h Pratt and Reid, *This Journal*, **57**, 37 (1937).

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

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 disproportionation of the mixed thioethers. We observed the formation of diphenyl sulfide and 1,2-diphenylethane 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.⁸ The Raney nickel was prepared as described in our previous paper.¹ Three representative experiments are presented below. The results are assembled in Table I.

Reaction of α -Naphthyl Thiobenzoate with "Hydrogen-free" Raney Nickel.—A solution of 13.7 g. of α -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*

vacuo. Two fractions, containing sulfur, were obtained, the first with a b. p. 135-137° (7 mm.), yield 1.1 g. or 22.9%; the second with a b. p. 175-185° (0.1 mm.); and a residue that solidified on cooling and after recrystallization from ethanol melted at 109-110° (di- α -naphthyl sulfide, m. p. 110°)⁹; yield, 1.45 g. or 19.5%. The second fraction was redistilled at 0.1 mm. and the fraction boiling between 175-177° 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° (phenyl α -naphthyl sulfide 41.8°),¹⁰ 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 thiobenzoate was added to a xylene suspension of about 45 g. of Raney nickel previously heated at 100° *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 "Hydrogen-free Raney Nickel."—A xylene solution of 15 g. of benzyl thiobenzoate was added to about 75 g. of Raney nickel previously heated at 200° *in vacuo* for two hours, the mixture 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 recrystallizations, melted at 40-41° (mixed m. p. with phenyl benzyl sulfide 40-41°, 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 sulfur-containing liquid (b. p. 160-169° (12 mm.)) was ob-

(6) A. Mailhe, *Compt. rend.*, **180**, 1111 (1925).

(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).

(9) F. Krafft and R. Schönherr, *Ber.*, **22**, 825 (1889).

(10) E. Bourgeois, *ibid.*, **28**, 2318 (1895).

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-containing 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° (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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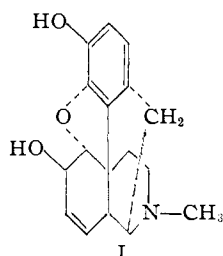
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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

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

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In a previous publication² it was pointed out that the Gulland and Robinson formula for morphine may be regarded as a substituted octahydroisoquinoline having an angular aryl group.³ 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.⁴ 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 corresponding lactone (IV) was formed.

Hydrogenation of III gave V in good yield.

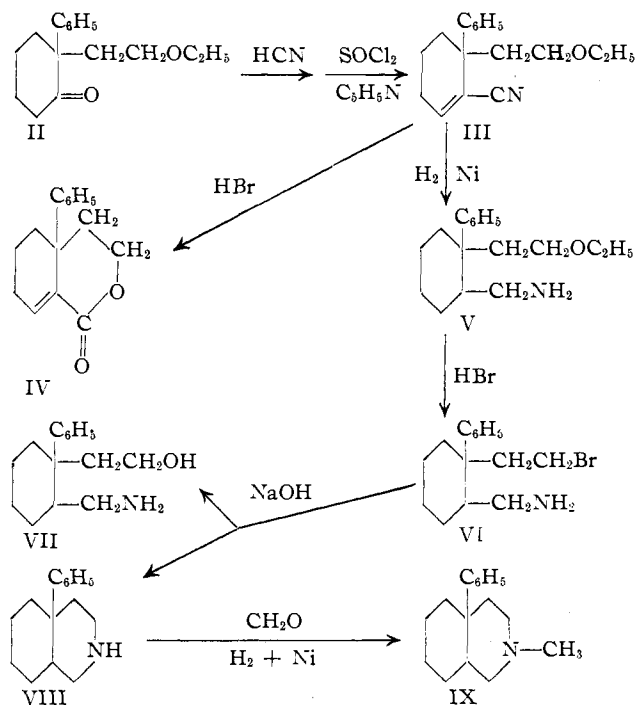
(1) (a) Sherman Clarke Fellow, 1948–1949; (b) present address: University of Illinois, Urbana, Illinois.

(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