

2. It has been shown that benzanisoin when reduced under suitable conditions produces not only *p*-methoxybenzyl phenyl ketone but also its isomer, benzyl *p*-methoxyphenyl ketone. Only the *anti* benzyl oxime was obtained from *p*-methoxybenzyl phenyl ketone.

3. By means of the Grignard reaction the structure of benzyl *p*-methoxyphenyl ketone has been determined by two independent methods.

4. A number of derivatives of benzanisoin has been obtained. A new carbinol was prepared and characterized.

5. The reliability of the method of Friedel and Crafts in structural work of this nature is brought into question.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, THE GOODYEAR TIRE & RUBBER Co.]

## THE REACTION OF DIAZONIUM SALTS ON SODIUM ALKYL DITHIOCARBAMATES

BY A. M. CLIFFORD AND J. G. LICHTY

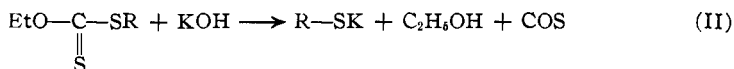
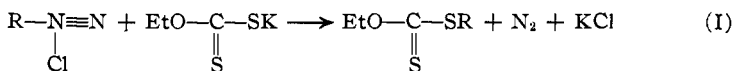
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Bernthsen and Friese<sup>1</sup> and also Billeter and Strohl<sup>2</sup> were apparently among the first to describe esters of disubstituted dithiocarbamic acids and reported the synthesis and properties of the ethyl and the phenyl esters of ethylphenyldithiocarbamic acid. Since these publications, little has appeared in the literature concerning this class of compounds. Certain nitro substituted aryl esters of dialkyl dithiocarbamic acids are claimed in patents issued to Cadwell,<sup>3</sup> and obtained by reaction between dithiocarbamate and an aryl compound containing reactive halogen.

A reaction has been found in this Laboratory which is capable of yielding the unsubstituted, as well as the substituted, aryl esters of alkyl dithiocarbamic acids.

Leuckart's excellent reaction<sup>4</sup> for the preparation of thiophenols sug-



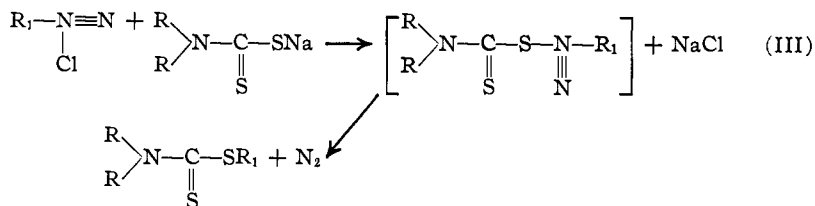
gested that diazonium salts should react in a manner similar to Equation I with alkyl dithiocarbamates, to yield the aryl ester of the dithiocarbamate

<sup>1</sup> Bernthsen and Friese, *Ber.*, **15**, 568 (1882).

<sup>2</sup> Billeter and Strohl, *ibid.*, **21**, 102 (1888).

<sup>3</sup> Cadwell, U. S. Patents, 1,726,646, 1,726,647, 1,726,648, Sept. 3, 1929; 1,736,429, Nov. 19, 1929.

<sup>4</sup> Leuckart, *J. pract. Chem.*, [2] **41**, 179 (1890).



That such a reaction does take place has been proved, and, furthermore, it provides a convenient method for obtaining such esters. It is the purpose of this paper to relate our experiences on the esterification of the dithiocarbamates derived from dimethylamine, diethylamine and piperidine by the above described reaction.

In Equation III postulated above an intermediate product is indicated as playing a part in the reaction. Good evidence for the formation of an intermediate, in most cases very unstable, product was the isolation of an explosive material from the reaction between sodium dimethyldithiocarbamate and *p*-nitrophenyldiazonium chloride. This material lost its detonating tendency after exposure in the open air for several hours, and on boiling in alcohol yielded *p*-nitrophenyldimethyldithiocarbamate. Königs<sup>5</sup> likewise has indicated that diazonium salts of certain acids may be isolated, for example, benzenediazonium benzene sulfinate,  $\text{C}_6\text{H}_5\text{N}_2\text{SO}_2\text{-C}_6\text{H}_5$ , which appears as a fairly stable compound.

### Experimental

**Preparation of Diazonium Salts.**—One mole of the amine and two moles of hydrochloric acid, using approximately 10% acid of known concentration, were diluted to 1500 cc. The solution was maintained at 0–5° and stirred during the addition of a solution of 2% excess of sodium nitrite in 300 cc. of water. At the end of the addition of the sodium nitrite a solid was formed. While this was not desirable it was unavoidable inasmuch as an excess of acid would decompose the dithiocarbamate during the coupling process.

**Preparation of Sodium Dithiocarbamates.**—A 20% aqueous solution containing one mole of the amine maintained at 10° or below was stirred during the slow addition of 1.05 moles of carbon disulfide. This was followed by the slow addition of one mole of sodium hydroxide of approximately 10% concentration. The product was then allowed to warm to room temperature. In the preparation of piperidiniumpentamethylenedithiocarbamate, water was added until the salt was completely dissolved. The aqueous solution was decanted from the excess carbon disulfide. This carbon disulfide was washed with water several times by decantation, adding the washings to the aqueous solution.

**Coupling.**—The cold aqueous solution of the diazonium salt was added in equimolecular proportion, dropwise, to the well-stirred aqueous dithiocarbamate solution at room temperature. Each drop of the diazonium solution added caused an immediate, violent evolution of nitrogen with only a small liberation of heat. The behavior on addition of *p*-nitrophenyldiazonium chloride, however, was an exception, as only a very small quantity of nitrogen was evolved, and a solid product separated which, when

<sup>5</sup> Königs, *Ber.*, 10, 1533 (1877).

dry, was explosive. In most instances the evolution of nitrogen was accompanied by the separation of a reddish-yellow oily layer. It was customary to allow the reaction mixture to stand for twelve to sixteen hours, during which time partial crystallization of the product usually occurred.

The crystalline portion of the reaction product was filtered off and washed with a small quantity of diethyl ether to remove adhering oil. The solid material thus obtained was a relatively pure ester. The liquid portion of the product was taken up with ether and to this solution was added the ether extracts of the aqueous layer. The ether solution was dried with calcium chloride, filtered and the solution evaporated by gentle warming, then set aside to crystallize. The crystals thus obtained were filtered off, washed as before, combined with the first crop, and the whole recrystallized from alcohol. Large white or pale yellow well-defined crystals were obtained. The *p*-tolyl esters in particular formed perfect, massive prisms of one centimeter or more across. The oily filtrate was subjected to distillation under reduced pressure; this process apparently caused partial decomposition as only after distillation was the odor of thiophenols noticeable. The fractions obtained usually solidified, completely or in part. Further purification of the various fractions by repeated crystallizations yielded the substituted ammonium dithiocarbamate, the disulfides and thioureas, in addition to more of the ester.

When a solid product was obtained by the interaction of the diazonium salt on the dithiocarbamate, it was removed by filtration, dried and separated into its various constituents by a series of fractional crystallizations.

Data pertaining to the compounds obtained by the above procedure are given in the table.

TABLE I  
PRODUCTS OF REACTION OF DIAZONIUM SALTS

Diazonium salt No.	derived from	Amine used Moles, g.	Yield of crude product, g.	(DTCB = dithiocarbamate) Miscellaneous compounds	M. p., °C.	
DERIVATIVES OF SODIUM DIMETHYLDITHIOCARBAMATE						
1	Aniline	1.2	111.6	209	Dimethylammonium dimethyl-DTCB Tetramethylthiourea Diphenyl disulfide (17 g.)	127-129 <sup>a</sup> 78-79 <sup>b</sup> 60-61 <sup>a</sup>
2	<i>p</i> -Toluidine	1.2	128.4	227.8		
3	<i>o</i> -Toluidine	1.2	128.4	193.2	Dimethylammonium dimethyl-DTCB Tetramethylthiourea	127-129 <sup>a</sup> 78-79
4	<i>p</i> -Bromoaniline	0.8	137.6	184.5	4,4'-Dibromodiphenyl disulfide	93-94 <sup>c</sup>
5	<i>p</i> -Nitroaniline	0.8	110.4	130.5		
DERIVATIVES OF SODIUM DIETHYLDITHIOCARBAMATE						
6	Aniline		93	193.2	Diethylammonium diethyl-DTCB	81-82 <sup>a</sup>
7	<i>p</i> -Toluidine		107	209.7	Diethylammonium diethyl-DTCB	81-82 <sup>a</sup>
DERIVATIVES OF SODIUM PENTAMETHYLENEDITHIOCARBAMATE						
8	Aniline		93	213.6	Diphenyl disulfide (0.4 g.) Piperidiniumpentamethylene-DTCB (8.8 g.)	60-61 <sup>a</sup> 169-170 <sup>a</sup>
9	<i>p</i> -Toluidine		107	226.5	Piperidiniumpentamethylene-DTCB (30.6 g.)	169-170 <sup>a</sup>

<sup>a</sup> These compounds when mixed with a pure sample synthesized by other methods gave no depression of the melting points.

<sup>b</sup> *Anal.* Calcd. for C<sub>8</sub>H<sub>12</sub>N<sub>2</sub>S: N, 21.21. Found: N, 20.86, 20.93. Delépine [*Bull. soc. chim.*, 7, 988-993 (1910)] reports a melting point of 78° for tetramethylthiourea.

<sup>c</sup> *Anal.* Calcd. for C<sub>12</sub>H<sub>8</sub>Br<sub>2</sub>S<sub>2</sub>: Br, 42.54. Found: Br, 42.00, 41.90. Hübner and Alsberg [*Ann.*, 156, 328 (1870)] reports a melting point of 93.5° for 4,4'-dibromodiphenyl disulfide.

TABLE I (Concluded)

No.	Ester (dithiocarbamate)	Yield, g.	M. p., °C.	Formula	Analyses					
					Nitrogen, %		Sulfur, %			
				Calcd.	Found	Calcd.	Found			
DERIVATIVES OF SODIUM DIMETHYLDITHIOCARBAMATE										
1	Phenyldimethyl-	75.5	94-95	$C_8H_{11}NS_2$	7.11	7.05	7.05	32.48	32.45	32.30
2	<i>p</i> -Tolyldimethyl-	64.5	112-113	$C_{10}H_{13}NS_2$	6.63	6.55	6.41	30.33	30.40	30.55
3	<i>o</i> -Tolyldimethyl-	46.5	81-82	$C_{10}H_{13}NS_2$	6.63	6.65	6.57	30.33	30.00	29.90
4	<i>p</i> -Bromophenyldi- methyl-	20	120-121	$C_9H_9NS_2Br$	5.09	5.10	5.10	23.19	23.15	23.30
5	<i>p</i> -Nitrophenyldi- methyl-	50.3	154	$C_8H_9O_2N_2S_2$	11.57	11.34	11.34	26.44	25.85	25.95
DERIVATIVES OF SODIUM DIETHYLDITHIOCARBAMATE										
6	Phenyldiethyl-	38.6	46	$C_{11}H_{15}NS_2$	6.22	6.15	6.08	28.44	28.30	28.40
7	<i>p</i> -Tolyldiethyl-	73.9	77-78	$C_{12}H_{17}NS_2$	5.86	5.83	5.81	26.77	27.00	26.90
DERIVATIVES OF SODIUM PENTAMETHYLENEDITHIOCARBAMATE										
8	Phenylpentamethy- lene-	78	116-117	$C_{12}H_{15}NS_2$	5.90	5.95	5.88	27.00	27.30	27.30
9	<i>p</i> -Tolylpentamethy- lene-	90.4	118-119	$C_{13}H_{17}NS_2$	5.57	5.46	5.32	25.50	25.85	25.95

Preliminary evidence indicates that nitrogen is retained in the reaction products of diazonium salts with the alkali metal salts of aliphatic and aromatic carboxylic acids.

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### Summary

1. Diazonium salts react with sodium alkyl dithiocarbamates, giving as the main product aryl esters of the dithiocarbamic acids.

2. A series of new aryl esters of dimethyl-, diethyl- and pentamethylenedithiocarbamic acids has been described.

3. Other compounds isolated from the reaction products include the aryl disulfides, the substituted ammonium alkyl dithiocarbamates and in some cases an alkyl substituted thiourea.

AKRON, OHIO