tion *ca.* 0.5 g. of a colorless liquid; b.p. 70° (28 mm.), n^{20}_D 1.4801.

Anal. Calcd. for C_9H_{16}: C, 87.02; H, 12.98. Found: C, 87.18; H, 12.82.

The infrared spectrum of this product (Fig. 3) showed strong absorption in the region 13.5–14.5 μ and no absorption at 10.25 μ indicating the substance to be XI.

This sample of XI when mixed with phenyl azide showed no observable reaction over a period of 2 weeks.

Cyclononanol (IX).—The reduction of 32.6 g. (0.023 mole) of II with lithium aluminum hydride gave 31 g. (94%) of distilled cyclononanol; b.p. 115–119° (15 mm.), n^{20}_D 1.4903.

Dehydration of IX.—Following a procedure previously described for the dehydration of cyclodecanol[1] 13.1 g. (0.09 mole) of IX was added to 45 g. of boiling phthalic anhydride. Distillation of the reaction product gave 8 g. of a colorless liquid: b.p. 51.3–53° (7 mm.), n^{20}_D 1.4776. This distillate was then chromatographed through silica gel. About 60% of the fractions thus obtained showed n^{20}_D 1.4792–1.4796. The infrared spectrum of this material (Fig. 3) showed characteristic absorption for both X and XI.

Anal. Calcd. for C_9H_{16}: C, 87.02; H, 12.98. Found: C, 87.05, 87.15; H, 12.83, 12.98.

Quantitative reduction of this mixture of cyclononenes in acetic acid using Adams catalyst required 98.91% of one molar equivalent of hydrogen.

Cyclononane.—The products obtained in the quantitative hydrogenation of the various samples of cyclononene were combined and distilled. The sample of cyclononane thus obtained showed b.p. 171–172.5° (740 mm.) (lit. gives b.p. 170–172° (760 mm.))[21] and n^{20}_D 1.4663. The infrared spectrum of this sample of cyclononane is shown in Fig. 2.

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[21] N. D. Zelinsky, *Ber.*, **40**, 3277 (1907).

ITHACA, N. Y.

[CONTRIBUTION FROM AMERICAN CYANAMID COMPANY, MINERAL DRESSING LABORATORY]

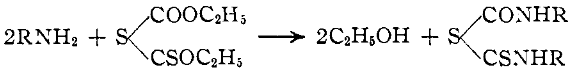
The Reaction of Arylamines with Diethyl Thionothiodiformate

BY RALPH SAYRE

RECEIVED JANUARY 10, 1952

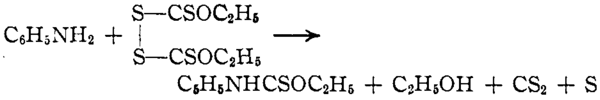
Diethyl thionothiodiformate reacts with arylamines to form ethyl arylthionocarbamates. Earlier investigators had erroneously formulated the products as diarylamides of thionothiodiformic acid.

By treating six aromatic monoamines with diethyl thionothiodiformate,[1] $C_2H_5O\underset{\underset{O}{\|}}{C}\text{-}S\text{-}\underset{\underset{S}{\|}}{C}OC_2H_5$, Guha and Dutta[2] claimed to have obtained a new series of compounds, to which they assigned the structure $RNH\underset{\underset{O}{\|}}{C}\text{-}S\text{-}\underset{\underset{S}{\|}}{C}NHR$, and which they designated as "thiodicarbomonothiodiarylamides.[3]" The reaction was carried out in each case at about 0° by adding the amine gradually to the ester dissolved in alcohol; the mixture was subsequently shaken with dilute hydrochloric acid in order to remove unreacted amine, and the solid product which separated at that point was filtered and crystallized from alcohol. In some instances Guha and Dutta added two moles of amine to one of ester, while in others the ratio was one to one. No information was given as to the yields obtained, nor was the reaction represented by an equation. The article seemed to imply, however, that the ethoxy groups were simply replaced by amine radicals.



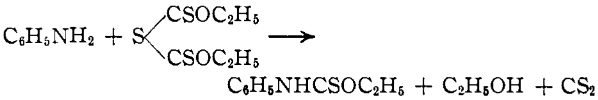
$$2RNH_2 + S\begin{matrix}\diagup COOC_2H_5\\ \diagdown CSOC_2H_5\end{matrix} \longrightarrow 2C_2H_5OH + S\begin{matrix}\diagup CONHR\\ \diagdown CSNHR\end{matrix}$$

Such behavior with amines is at variance with that of other xanthic acid derivatives structurally related to diethyl thionothiodiformate. Hofmann[4] obtained ethyl phenylthionocarbamate as the principal product of the reaction between aniline and diethyl dithiobis-(thionoformate)[5]



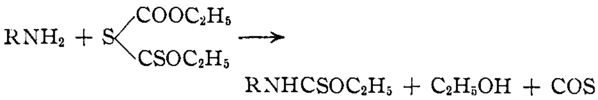
$$C_6H_5NH_2 + \begin{matrix}S\text{—}CSOC_2H_5\\ |\\ S\text{—}CSOC_2H_5\end{matrix} \longrightarrow C_6H_5NHCSOC_2H_5 + C_2H_5OH + CS_2 + S$$

In 1928 the present writer[6] similarly treated aniline with the monosulfide, diethyl thiobis-(thionoformate),[7] and has subsequently used the reaction



$$C_6H_5NH_2 + S\begin{matrix}\diagup CSOC_2H_5\\ \diagdown CSOC_2H_5\end{matrix} \longrightarrow C_6H_5NHCSOC_2H_5 + C_2H_5OH + CS_2$$

for the preparation of the corresponding esters from *o*-toluidine, α-naphthylamine, N-ethylaniline and cyclohexylamine. The reaction of amines with diethyl thionothiodiformate might reasonably be expected to proceed in an analogous manner, forming carbonyl sulfide instead of carbon disulfide as a by-product. It is noteworthy that



$$RNH_2 + S\begin{matrix}\diagup COOC_2H_5\\ \diagdown CSOC_2H_5\end{matrix} \longrightarrow RNHCSOC_2H_5 + C_2H_5OH + COS$$

Guha and Dutta applied the reaction to phenylhydrazine, which they had expected to yield a "diphenylhydrazide," and obtained instead ethyl 2-phenylthionocarbazate[8]; accordingly they repre-

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[1] "Ethylxanthogen ethylformate," first made by B. Holmberg, *J. prakt. Chem.*, [2] **71**, 264 (1905). The complex xanthic acid esters referred to in this paper are named as thionoformic acid derivatives in conformity with *C. A.* nomenclature (Coll. Form. Index, pp. 134 and 135).

[2] P. C. Guha and D. N. Dutta, *J. Indian Chem. Soc.*, **6**, 65 (1929); abstracted in *Brit. Chem. Abstracts A*, 583 (1929); *Chem. Zentr.*, 100, I, 2779 (1929); *C. A.*, **23**, 2952 (1929).

[3] Beilstein, 2nd Suppl. XII, lists four of the products as arylaminoformylarylaminothioformyl sulfides and two of them as tolylcarbamic acid-tolyldithiocarbamic acid anhydrides.

[4] A. W. Hofmann, *Ber.*, **3**, 774 (1870).

[5] "Dixanthogen" or "bisethylxanthogen," first made by P. Desains, *Ann. chim.*, [3] **20**, 504 (1847).

[6] Unpublished work.

[7] "Ethylxanthic anhydride," first made by H. Welde, *J. prakt. Chem.*, [2] **15**, 45 (1877).

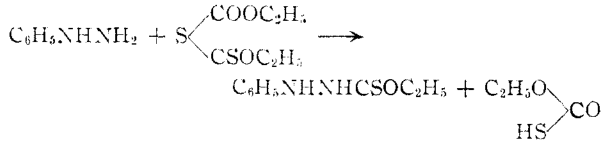
[8] No reference was made to the previous preparation of this compound by H. L. Wheeler and B. Barnes, *Am. Chem. J.*, **24**, 65 (1900).

TABLE I

Arylamines	Guha and Dutta Products RNHCOSCSNHR					Ethyl Arylthionocarbamates $RNHCSOC_2H_5$				
	Calculated		Found		M.p., °C.	Calculated, %		Literature, m.p., °C.	Present work	
R =	N, %	S, %	N, %	S, %		N	S		M.p., °C.	Yield, %
Phenyl	9.71		9.82		63–64	7.73		68–69[a]; 69[b]; 71–72[c]	68–69	87
o-Tolyl	8.86		8.91		205	7.18		37[d]	35–36	59
p-Tolyl	8.86	20.25	8.52	20.81	85	7.18	16.42	85[e,f]; 87[g]	84–85	70
m-Nitrophenyl	14.81		14.52		105	12.38		115[e,h]	114–115	65
p-Nitrophenyl	14.81		14.65		95–96	12.38		175[e,f]; 175–176[i]; 177–178[j]	177–178	35
β-Naphthyl	7.21		7.05		90	6.06		92[k]; 96–97[l]	96–97	73

[a] E. Bamberger, *Ber.*, **15,** 2164 (1882); E. Fromm, *ibid.*, **42,** 1957 (1909). [b] E. Biilmann, *Ann.*, **348,** 141 (1906). [c] C. Liebermann, *ibid.*, **207,** 145 (1881). [d] J. R. Bailey and A. T. McPherson, THIS JOURNAL, **38,** 2526 (1916). [e] D. W. Browne and G. M. Dyson, *J. Chem. Soc.*, 3307 (1931). [f] R. W. Bost and E. R. Andrews, THIS JOURNAL, **65,** 901 (1943). [g] C. Liebermann, *Ann.*, **207,** 160 (1881). [h] S. M. Losanitsch, *Ber.*, **16,** 49 (1883); H. Steudemann, *ibid.*, **16,** 550 (1883). [i] S. M. Losanitsch, *ibid.*, **15,** 471 (1882). [j] P. Jacobson and J. Klein, *ibid.*, **26,** 2369 (1893). [k] D. W. Browne and G. M. Dyson, *J. Chem. Soc.*, 179 (1934). [l] C. Cosiner, *Ber.*, **14,** 62 (1881).

sented the reaction in substantially the manner indicated above



$$C_6H_5NHNH_2 + S\begin{cases}COOC_2H_5\\CSOC_2H_5\end{cases} \longrightarrow C_6H_5NHNHCSOC_2H_5 + \begin{matrix}C_2H_5O\\HS\end{matrix}\!\!>CO$$

As shown in Table I, the melting points of four of the "diarylamides" agree at least approximately with literature values for the corresponding ethyl arylthionocarbamates; anomalous melting points were found by Guha and Dutta for the *o*-tolyl and *p*-nitrophenyl derivatives. The table also presents their analytical data consisting of one sulfur and six nitrogen determinations, all of which support the "diarylamide" structure and can hardly be reconciled with the calculated values shown for the arylthionocarbamates. In view of the analytical and melting point discrepancies, the Guha and Dutta reaction was carried out with each of the six amines, and in every case the expected ethyl arylthionocarbamate was obtained.

The Guha and Dutta procedure was used in treating diethyl thionothiodiformate with aniline and with *o*-toluidine. In both cases, measurement of excess amine by acid titration showed that the reaction involved only one mole of amine per mole of thionothiodiformate. In addition to ethyl *o*-tolylthionocarbamate, which separated initially as a liquid, the *o*-toluidine reaction mixture yielded the solid product isolated by Guha and Dutta; it was the only one of their six "diarylamides" not specifically stated to be soluble in alkali and insoluble in acid. In the present work, the substance was identified as *o*-toluidine hydrochloride, which melts at 214.5–215°[9] and contains 9.75% nitrogen.

Preliminary experiments with the two nitroanilines showed that they reacted very slowly with diethyl thionothiodiformate under the conditions prescribed by Guha and Dutta. This was especially true of *p*-nitroaniline, so that the crude product was badly contaminated with unreacted amine. The comparative difficulty of purification may well explain the fact that their melting point was about 80° too low. In subsequent experiments, excess diethyl thionothiodiformate was used, and the reaction mixtures were heated in a steam-bath. Even under these conditions, *p*-nitroaniline reacted quite slowly, whereas *m*-nitroaniline was rapidly converted to the thionocarbamate. Excess diethyl thionothiodiformate was also used in the *p*-toluidine and *β*-naphthylamine reactions, both of which proceeded rather vigorously at room temperature. It was necessary, in fact, to moderate the reactions somewhat in order to control the effervescence due to escaping carbonyl sulfide.

Guha and Dutta stated that "the diarylamides form diacetyl derivatives," but cited only one, that of their alleged "thiodicarbomonothiodi-*m*-nitranilide": "The diacetyl derivative was obtained by heating the substance for a short time with an excess of acetic anhydride. It crystallized from alcohol, m.p. 114–115°. (Found: N, 12.42. $C_{18}H_{14}O_7N_4S_2$ requires N, 12.12.)" It seems fairly obvious that their initial product, melting at 105°, was merely freed from impurities by this additional treatment, so that its melting point was raised to the correct value. This conjecture is substantiated by the nitrogen content, which is in excellent agreement with the calculated value shown for the nitrophenylthionocarbamates. For even more conclusive evidence on this point, specimens of the pure phenyl and *m*-nitrophenyl derivatives obtained in the present work were heated with excess acetic anhydride and were recovered substantially unchanged in weight and in melting point.

Details are given only for the preparation of the phenyl derivative, the elementary microanalysis of which was carried out in these laboratories under the direction of Dr. J. A. Kuck.

Experimental

Diethyl thionothiodiformate was prepared by the method of Holmberg[1] and distilled at 1 mm. pressure through a 27-cm. fractionating column packed with Pyrex helices. The 84–94° fraction was used in this work.

Ethyl Phenylthionocarbamate.—A solution of 19.4 g. (0.1 mole) of diethyl thionothiodiformate in 25 ml. of alcohol was cooled in an ice–salt-bath and stirred mechanically while 20.0 g. (0.215 mole) of aniline was added dropwise. Evolution of considerable heat and separation of a crystalline product occurred during the addition of the first half; no indication of an exothermic reaction was observed thereafter. The mixture was stirred three hours longer and brought to slight acidity by the gradual addition of 38 ml. of 3 *N* HCl (0.114 mole), showing that only 0.1 mole of aniline had reacted. The slurry was diluted with 100 ml. of water, cooled to 1°, and filtered. The colorless filter-cake, after being washed with water and air-dried, weighed 15.8 g. and melted at 63–64°. One recrystallization from ether

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[9] F. Ullmann, *Ber.*, **31,** 1699 (1898).

raised the m.p. to 68–69°, unchanged when the substance was mixed with a like amount of an authentic specimen of ethyl phenylthionocarbamate.

Anal. Calcd. for $C_9H_{11}NOS$: C, 59.63; H, 6.12; N, 7.73; S, 17.69; $-OC_2H_5$, 24.86. Found: C, 59.52, 59.77; H, 6.25, 6.18; N, 7.97, 7.81; S, 17.41, 17.53; $-OC_2H_5$, 24.87, 24.82.

STAMFORD, CONN.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE POLYTECHNIC INSTITUTE OF BROOKLYN AND FROM THE WELLCOME RESEARCH LABORATORIES]

The Effect of Substitution on the Solvolysis Rates of Benzhydryl Chlorides[1]

BY SIEGFRIED ALTSCHER,[2] RICHARD BALTZLY AND SAMUEL W. BLACKMAN

RECEIVED JANUARY 21, 1952

Solvolysis rates of a number of substituted benzhydryl chlorides have been studied in methanol and in isopropyl alcohol. The influence of substituents is in general accord with theoretical expectations. The effect of two or more substitutions appears to be reasonably predictable from that of the individual substituents separately.

Norris[3] and his collaborators have determined the solvolysis rates of a number of benzhydryl chlorides. The reaction had already been shown to be independent of the concentration of base[4] and is now recognized as a typical SN1 displacement. The conductometric method of Norris has been subject to some criticism and certain reaction constants, notably for benzhydryl chloride itself and its alkyl substituents, have been revised by subsequent workers[5–7] but no comparable survey has since been made of the effect of substitution on the rate of solvolysis. The Norris figures for monosubstituted benzhydryl chlorides are in general agreement with expectations based on the modern theories of displacement reactions. The only solvolysis rate available for a disubstituted benzhydryl chloride was also determined by Norris who found k-relative ($= k/k$ unsubstituted) for 4,4′-dichlorobenzhydryl chloride to be 0.15—very nearly the square of k-relative for *p*-chlorobenzhydryl chloride (0.4).

As a number of substituted benzhydryl chlorides or their precursors were available through certain synthetic activities,[8,9] it was decided to extend the earlier series of Norris to ascertain what regularities could be found in the behavior of polysubstituted compounds.

Experimental

Since the variation in reaction rates among substituted benzhydryl chlorides is so great that no single solvent is convenient for all cases, it was decided to run the more reactive compounds in isopropyl alcohol and the less reactive in methanol. Rates were determined for benzhydryl chloride, *p*-chlorobenzhydryl chloride and 4,4′-dichlorobenzhydryl chloride in both solvents. Reactions were run in duplicate except when more determinations were required and were followed to at least 20% completion; in most cases to 60–70%.

Determination of Reaction Rates.—Enough of the benzhydryl chloride to give a solution 0.05–0.15 molar was weighed into a volumetric flask, made up to volume with the desired solvent and thermostated at 25.00 ± 0.05°. As soon as possible after mixing, an aliquot was removed for a zero point titration. Since in a number of cases the purity of the benzhydryl chlorides could not be established, in all cases one or more aliquots were subjected to complete solvolysis by addition to aqueous methanol in a glass-stoppered flask, and titrated after a suitable time with standard alkali. The value so obtained was taken as the initial concentration of the benzhydryl chloride. For the actual titrations during the run, the aliquots were pipetted into acetone to "freeze" the reaction and titrated with standard alkali. Hughes, Ingold and Taher[7] give this as their general procedure but since we have found that in practice further details are necessary, the following procedure is given.

One-cc. aliquots (of an original 25 cc. of reaction mixture) were pipetted into 20–25 cc. of acetone. Indicator (methyl red–methylene blue) was added and the greater part of the alkali expected to be necessary. Water was then added cautiously until the indicator gave a purple color and the titration was completed by adding alkali dropwise at about one drop per second with constant agitation until the solution became a clear, sparkling green.

The fundamental difficulty is that although a very large excess of acetone stops the solvolysis, indicators do not behave properly in such solutions. With most of these reactions effective "freezing" during the time of titration could be achieved. However, the more rapidly reacting substances (in this study, those with *p*-methoxyl substitution) cannot be "frozen" properly under conditions permitting titration. Rates obtained with these substances cannot be regarded as more than approximate even though in certain instances the usual mathematical treatment shows a high degree of "precision."

Materials.—Most of the benzhydryl chlorides or their precursors were available from previous work.[8,9] All the benzhydryl chlorides have been employed in synthetic operations and have been converted to crystalline substances of known composition. The procedure of Norris and Blake[3c] is adequate for conversion of most of the carbinols to chlorides; it is not adequate with the carbinols that react least rapidly—presumably corresponding to the least active benzhydryl chlorides.

The *o*- and *m*-chloro-, 2,4- and 3,4-dichloro-, 2,4,4′-trichloro- and *p*-nitrobenzhydryl chlorides were accordingly prepared by warming the appropriate carbinols with excess thionyl chloride and a few drops of pyridine. After several hours heating on the steam-bath, thionyl chloride was removed *in vacuo*, toluene was added and removed *in vacuo* (twice). The residues were then taken up in hexane, filtered and evaporated. The crude oils were then distilled *in vacuo* (0.01–0.03 mm.).

Of the various benzhydryl chlorides, 4,4′-dichlorobenz-

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[1] Taken in part from a thesis submitted by S. Altscher to the Department of Chemistry of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of M.S. in chemistry, June, 1950.

[2] Appreciation is expressed to Wallace and Tiernan Products, Inc., for facilities granted to one of us (S. A.) during the course of this work.

[3] (a) J. F. Norris and A. A. Morton, THIS JOURNAL, **50**, 1795 (1928); (b) J. F. Norris and C. Banta, *ibid.*, **50**, 1804 (1928); (c) J. F. Norris and J. T. Blake, *ibid.*, **50**, 1808 (1928).

[4] A. M. Ward, *J. Chem. Soc.*, 2285 (1927).

[5] F. G. Kny-Jones and A. M. Ward, THIS JOURNAL, **57**, 2394 (1935).

[6] N. T. Farinacci and L. P. Hammett, *ibid.*, **59**, 2542 (1937).

[7] E. D. Hughes, C. K. Ingold and N. A. Taher, *J. Chem. Soc.*, 949 (1940).

[8] L. P. Albro, R. Baltzly and A. P. Phillips, *J. Org. Chem.*, **14**, 771 (1949).

[9] R. Baltzly, S. DuBreuil, W. Ide and E. Lorz, *ibid.*, **14**, 775 (1949).