and 50 lb. of hydrogen pressure were used in each case. With ester II and platinum oxide catalyst, the reaction was complete in twenty minutes; with palladous oxide, the reaction required four hours. Ester III was reduced in two to four hours using platinum and, incompletely, after seven hours with palladium.

The saturated ester (IV) was recovered upon fractionation of the alcoholic solution and identified by its boiling point, density and refractive index.[14]

Degradation of High Boiling Ester (III).—Seven grams (0.05 mole) of the ester, boiling at 169°, was treated with 0.05 mole of hydrogen peroxide and 2 ml. of osmium tetroxide catalyst according to the procedure of Milas and Sussman.[11] The gray solution was distilled under diminished pressure. The fraction boiling from 62 to 73° contained the glycol (VII). This was treated with successive small portions of perchlorato-cerate ion in perchloric acid, "Ceric perchlorate,"[12] (10 g. $(NH_4)_2Ce(NO_3)_6$ in 50 ml. of 15 to 20% perchloric acid) until a red color was no longer formed. Air was blown through the warmed solution and then into a test-tube containing 2,4-dinitrophenylhydrazine dissolved in dilute perchloric acid. The bright yellow crystals which precipitated were collected, washed and crystallized twice from ethanol; m. p. 124–126°. A mixed melting point with an authentic sample of propanone-2,4-dinitrophenylhydrazone gave no depression.

After all the propanone had been blown out of the reaction mixture, addition of a perchloric acid solution of 2,4-dinitrophenylhydrazine produced a precipitate which melted at 221.5 to 223.5° after one crystallization from dioxane–ethanol. A mixed melting point with an authentic sample of 2-keto-propanoic acid 2,4-dinitrophenylhydrazone (m. p. 221.5–223°) gave no depression.

Degradation of Low Boiling Ester (II).—Hydroxylation of the ester boiling at 151° was carried out as above. However, the glycol began to decompose at 70° at 13 mm. Hence, the residue was treated with the "ceric perchlorate" as previously described. As soon as the "ceric perchlorate" no longer gave a red color, the solution was made alkaline with potassium hydroxide and refluxed three to four hours. Air was blown through the solution as before. The precipitated 2,4-dinitrophenylhydrazone, upon recrystallization from ethanol, melted at 108–109°. No depression in the melting point was observed when this compound was mixed with an authentic sample of butanone 2,4-dinitrophenylhydrazone.

Acknowledgment.—We wish to express our appreciation to Dr. Frederick R. Duke for his suggestions concerning the use of "ceric perchlorate" in splitting the glycols obtained during this investigation.

Summary

Ethyl 3-hydroxy-2,3-dimethylbutanoate has been dehydrated to ethyl 2,3-dimethyl-2-butenoate and ethyl 2,3-dimethyl-3-butenoate. These have been isolated and their physical constants determined.

The structure of these unsaturated esters has been assigned on the basis of the ketones to which they have been degraded.

East Lansing, Michigan Received July 5, 1946

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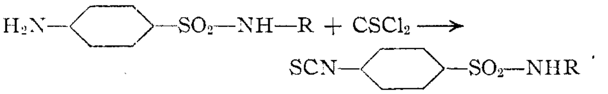
[14] Gorski, *J. Russ. Phys.-Chem. Soc.*, **45**, 167 (1912).

[Contribution from the Venable Chemical Laboratory of the University of North Carolina]

p-Substituted Phenyl Isothiocyanates and Some Related Thioureas

By R. L. McKee[1] and R. W. Bost

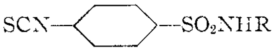
By use of the reaction between primary amines and thiophosgene,[2] sulfanilamide, sulfadiazine, sulfaguanidine, sulfacetamide, sulfapyridine and sulfathiazole have been converted into the corresponding isothiocyanates (Table I).



The isothiocyanates are quite stable in contact with water or dilute aqueous acids. They may be dissolved in cold, dilute alkali and reprecipitated unchanged by acid; prolonged solution in alkali brings about their decomposition.

Several of the isothiocyanates and the previously prepared[2] *p*-isothiocyanobenzoic acid were allowed to react with amines to form the corresponding thioureas (Table II).

Table I

p-Isothiocyanobenzenesulfonamides,


Cpd.	R=	Sulfonamide	Moles	Cryst. from	Yield pure product, %	M. p., °C.	Formula	Analyses, % sulfur Calcd.	Analyses, % sulfur Found
I	Hydrogen	Sulfanilamide	0.12	Acetone–water	89	212–214 (dec.)	$C_7H_6N_2O_2S_2$	29.93	29.84
II	Acetyl	Sulfacetamide	.095	Acetone–ligroin	88	156–159	$C_9H_8N_2O_3S_2$	25.02	24.98
III	Carboxamidine	Sulfaguanidine	.035	Acetone–water	76	216–217	$C_8H_8N_4O_2S_2$	25.02	24.81
IV	2-Pyridyl	Sulfapyridine	.16	Acetone–dioxane	90	198–200 (dec.)	$C_{12}H_9N_3O_2S_2$	22.01	22.07
V	2-Thiazolyl	Sulfathiazole	.16	Acetone	98	239–242 (dec.)	$C_{10}H_7N_3O_2S_3$	32.34	32.19
VI	2-Pyrimidyl	Sulfadiazine	.064	Dioxane–water	95	237–240 (dec.)	$C_{11}H_8N_4O_2S_2$	21.93	22.02

The exclusive attack on the amino nitrogen is indicated by the high yields of products which have retained the characteristic alkali solubility of sulfonamides but are no longer acid soluble.

Experimental

Since identical procedures were employed for each of the two groups comprising compounds I-VI and VII-XII, only one preparation from each group is described in detail.

4-Isothiocyanobenzenesulfonamide (I).—Sulfanilamide (20 g., 0.12 mole) was dissolved in 200 cc. of water con-

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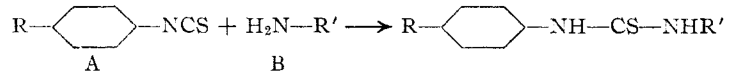
[1] The Wm. S. Merrell Co., Postdoctoral Fellow.

[2] Browne and Dyson, *J. Chem. Soc.*, 178 (1934).

TABLE II



Cpd.	R, reagent A	R″, reagent B	Yield, %	M. p., °C.	Formula	Analyses, % sulfur Calcd.	Found
VII	Carboxy[a]	*p*-Sulfonamidophenyl[b]	94	213–215; 263–268 (dec.)[c]	$C_{14}H_{13}N_3O_4S_2$	18.25	18.17
VIII	Carboxy[a]	*p*-Sulfon-(2-thiazolyl)-amidophenyl[d]	71	185; 195–200 (dec.)[c]	$C_{17}H_{14}N_4O_4S_3$	22.14	22.11
IX	Carboxy[a]	*p*-Sulfon-(2-pyridyl)-amidophenyl[d]	84	175–179 (dec.)	$C_{19}H_{16}N_4O_4S_2$	14.96	14.97
X	Sulfonamido	*p*-Sulfon-(2-thiazolyl)-amidophenyl[e]	90	214–217 (dec.)	$C_{16}H_{15}N_5O_4S_4$	27.31	27.22
XI	Sulfonamido	6-Methoxy-8-quinolyl[e]	98	189–190 (dec.)	$C_{17}H_{16}N_4O_3S_2$	16.51	16.61
XII	Sulfon-(2-pyridyl)-amido	2-Thiazolyl[f]	82	167–170	$C_{15}H_{13}N_5O_2S_3$	24.57	24.51

[a] Browne and Dyson, ref. 2. [b] Recrystallized from dioxane–acetone. [c] Melted at 213–215°, resolidified and remelted at higher temperature. [d] Recrystallized from dioxane–water. [e] Due to extreme insolubility in organic solvents, the compound was dissolved in dilute sodium hydroxide, treated with norite, reprecipitated slowly with dilute acid, filtered and washed thoroughly with water, alcohol and acetone. [f] Reaction medium, dioxane–acetone; recrystallized as in *e*.

taining 50 cc. of concentrated hydrochloric acid. To this 13.4 g. (0.12 mole) of thiophosgene was added in one portion. Stirring was begun immediately and continued until all of the red color of thiophosgene had disappeared and the product appeared as a white crystalline precipitate. This was filtered, washed thoroughly with water, and recrystallized from acetone–water. The product consisted of 22 g. of white platelets melting with decomposition at 212–214°.

4-Carboxy-4′-sulfonamido-thiocarbanilide (VII).—Twenty grams (0.11 mole) of *p*-isothiocyanobenzoic acid[2] and 20 g. (0.12 mole) of sulfanilamide were dissolved in 800 cc. of dry acetone and refluxed for forty hours. (During this time it became necessary to remove the product several times by filtration to avoid severe bumping.) The "crude" product so obtained was recrystallized from dioxane–acetone; however, its melting point was not altered by this treatment. The thiourea so obtained consisted of 37 g. of a fine white powder. On heating, the product melted at 213–215° and immediately resolidified. Final melting with decomposition occurred at 263–268°.

Acknowledgment.—The authors wish to take this opportunity to express their appreciation to The Wm. S. Merrell Co., whose generous support made this work possible.

Summary

Six new aromatic isothiocyanates and six new thioureas, all derived from pharmacologically well-known sulfonamides, have been prepared and characterized.

CHAPEL HILL, NORTH CAROLINA
RECEIVED JUNE 24, 1946

[CONTRIBUTION FROM THE FOREST PRODUCTS LABORATORY,[1] FOREST SERVICE, U. S. DEPARTMENT OF AGRICULTURE]

Hydrogenation of Lignin over Raney Nickel[2]

BY J. F. SAEMAN AND E. E. HARRIS

The hydrogenation of lignin in dioxane solution over copper–chromium oxide has been carried out by Harris, D'Ianni and Adkins[3] and subsequently by others.[4,5] A number of new compounds of theoretical and practical interest resulted from their work. In this paper is described an investigation of the hydrogenation of methanol lignin over Raney nickel performed at the Forest Products Laboratory.

Raney nickel promotes greater activity toward aromatic structures than does copper chromium oxide. It was believed that this would lead to the formation of hydroaromatics from which structurally significant ether linkages would be less easily cleaved. Early experiments were carried out with the lignin in dioxane solution at temperatures below 210°, but no significant yield of volatile products was formed. Experiments with this solvent were discontinued because an explosive decomposition of the dioxane is liable to occur[6] at higher temperatures.

An absorption of 1 mole of hydrogen per 45 g. of lignin was obtained in ethanol at a temperature of 240,° but the product was almost exclusively a resin with a very high boiling point. At higher temperatures the ethanol is decomposed.

To avoid the complications caused by unstable solvents, lignin was hydrogenated, using water and hydrocarbons as non-solvent vehicles. In such liquids the lignin melts and reacts in the liquid phase. As hydrogenation progresses, part or all of the products may go into solution, depending on the nature of the vehicle. Advantages in speed and economy of catalyst result from the use of a hydrogen donor vehicle, such as decahydronaphthalene. In aqueous systems the use of alkali has a protective effect on the catalyst,[7] but it results in the production of more complex mixtures.

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(1) Maintained at Madison, Wisconsin, in coöperation with the University of Wisconsin.

(2) Abstracted from a thesis submitted by J. F. Saeman to the Faculty of the University of Wisconsin in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1942.

(3) E. E. Harris, J. D'Ianni and H. Adkins, THIS JOURNAL, **60**, 1467 (1938).

(4) H. Adkins, R. L. Frank and E. S. Bloom, *ibid.*, **63**, 549–555 (1941).

(5) J. R. Bower, L. M. Cooke and H. Hibbert, *ibid.*, **65**, 1192–1195 (1943).

(6) N. L. Drake, ed., "Organic Syntheses," John Wiley & Sons, Inc., New York, N. Y., 1941, Vol. 21, p. 16.

(7) E. E. Harris, J. F. Saeman and E. C. Sherrard, *Ind. Eng. Chem.*, **32**, 440 (1940).