

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NORTH CAROLINA]

4-PARA-TOLYLTHIOSEMICARBAZIDE AND ITS REACTIONS WITH KETONES

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In spite of the fact that many substituted semicarbazides have been studied with aldehydes and ketones, it appears that the substituted thiosemicarbazides have received little attention. In view of this, we have chosen for study a substituted thiosemicarbazide which is easy to prepare, gives a good yield, and whose raw materials are fairly cheap. It was condensed with the following ketones: acetone, methyl ethyl ketone, acetylacetone, ethyl acetoacetate, cyclohexanone, acetophenone, benzophenone, benzoylacetone, benzoin, benzil and carvone.

Experimental

Di-*p*-tolylthiourea.—A method similar to that of Sell¹ was used to prepare di-*p*-tolylthiourea. An alcoholic solution of *p*-toluidine was heated under reflux for five hours with an equivalent of carbon disulfide. The pure product melted at 177°; yield, 95%.

***p*-Tolyl Mustard Oil.**—The di-*p*-tolylthiourea was converted into *p*-tolyl mustard oil by heating the former with acetic anhydride under reflux for fifteen minutes. The product was poured into water, steam distilled, extracted with ether and redistilled; b. p. 237°; yield, 72%.

4-*p*-Tolylthiosemicarbazide.—The method of Guba and Ray² was adopted. An alcoholic solution of *p*-tolyl mustard oil, cooled in an ice-bath, was treated with 42% hydrazine hydrate. The bottle containing the mixture was stoppered and shaken for a few minutes. The product was filtered and purified from alcohol. The pearly white needles melted at 137°; yield, 90%.

4-*p*-Tolylthiosemicarbazide Hydrochloride.—Two grams of the semicarbazide was dissolved in 20 ml. of alcohol and 5 ml. of concentrated hydrochloric acid added. On cooling, long white needles separated; m. p. 173°; yield, 90%.

Anal. Calcd. for C₉H₁₂N₃ClS: HCl, 16.60. Found: HCl, 16.46.

Condensation Products

To 0.01 mole of 4-*p*-tolylsemicarbazide dissolved in 10 ml. of alcohol was added an equivalent of the ketone. In the case of benzophenone, benzoin, benzil and carvone, 1 ml. of glacial acetic acid was added at this point. The solution was placed under reflux and heated with a hot-plate. The time of heating of the mixture depended upon the ketone. The reaction product was cooled, filtered, dried and recrystallized from alcohol. With the exception of methyl ethyl ketone and benzoylacetone, the products on cooling formed solids; even the products from these ketones, when dried and recrystallized, gave definite solids. The condensation products are also soluble in benzene and chloroform. All are soluble in ether with the exception of those from acetylacetone, benzophenone and benzoylacetone.

¹ Sell, *Ann.*, **126**, 160 (1863).

² Guba and Ray, *THIS JOURNAL*, **47**, 385 (1925).

Alcoholysis of Acetylacetone-4-*p*-tolylthiosemicarbazone.—Wheeler and Norton³ have shown that acetylacetone phenylsemicarbazide yields 3,5-dimethylpyrazole and phenylurethan when refluxed with absolute alcohol. It was found that acetylacetone-4-*p*-tolylthiosemicarbazone behaves similarly when subjected to alcoholysis.

Three-tenths gram of acetylacetone-4-*p*-tolylthiosemicarbazone was dissolved in 10 ml. of absolute alcohol and refluxed for one hour. The alcohol was evaporated on a steam-bath, leaving a colorless oil which crystallized on cooling. The residue was extracted with 5 ml. of water. A small quantity of yellow oil was insoluble. The water solution was evaporated to 1 ml. on a steam-bath. On standing overnight, small colorless flakes of 3,5-dimethylpyrazole appeared. They melted at 105–106°. The oil insoluble in water was crystallized from petroleum ether, whereupon a small quantity of a crystalline substance melting at 69–74° was obtained. It possessed an odor similar to that of anisole. The substance was undoubtedly *p*-tolylthiourethan. No analysis could be made because of a lack of sufficient material.

TABLE I
DATA ON DERIVATIVES

| No. | Ketone | Form | Solvent | M. p., °C. |
|-----|---------------------|----------------------------|---------|------------------|
| 1 | Acetone | Colorless plates | Alcohol | 142 ⁴ |
| 2 | Methyl ethyl | Colorless plates | Alcohol | 75 |
| 3 | Acetylacetone | Fine white needles | Alcohol | 100 |
| 4 | Ethyl aceto-acetate | Fine white needles | Alcohol | 107 |
| 5 | Cyclohexanone | Long white needles | Alcohol | 125 |
| 6 | Acetophenone | Bulky white needles | Alcohol | 165 |
| 7 | Benzophenone | Pale yellow needles | Alcohol | 158 |
| 8 | Benzoylacetone | Pale yellow plates | Alcohol | 126 |
| 9 | Benzoin | Cream-colored needles | Alcohol | 161 |
| 10 | Benzil | Fine cream-colored needles | Alcohol | 164 |
| 11 | Carvone | Fine cream-colored needles | Alcohol | 147 |

| No. | Time heated, minutes | Formula | Sulfur analyses, % | |
|-----|-------------------------|---------------------------------------------------|--------------------|--------------------|
| | | | Calcd. | Found |
| 1 | 1 | C ₁₁ H ₁₆ N ₃ S | 14.48 | 14.65 ⁴ |
| 2 | 10 | C ₁₂ H ₁₇ N ₃ S | 13.52 | 13.68 |
| 3 | 5 | C ₁₃ H ₁₇ ON ₃ S | 12.09 | 11.99 |
| 4 | 15 | C ₁₄ H ₁₈ N ₃ S | 10.86 | 10.79 |
| 5 | 15 | C ₁₄ H ₁₈ N ₃ S | 12.18 | 12.24 |
| 6 | 15 | C ₁₆ H ₁₇ N ₃ S | 11.24 | 11.17 |
| 7 | 120 | C ₂₀ H ₁₉ N ₃ S | 9.23 | 9.32 |
| 8 | 15 | C ₁₈ H ₁₉ N ₃ S | 9.80 | 9.85 |
| 9 | 60 | C ₂₂ H ₂₁ ON ₃ S | 8.50 | 8.39 |
| 10 | 120 | C ₂₂ H ₁₉ ON ₃ S | 8.55 | 8.52 |
| 11 | 45 | C ₂₃ H ₂₆ N ₃ S | 10.17 | 10.25 |

Conclusions

1. 4-*p*-Tolylthiosemicarbazide has been prepared in good yields.
2. It was condensed with the following ketones: acetone, methyl ethyl ketone, acetylacetone, ethyl acetoacetate, cyclohexanone, acetophenone, benzophenone, benzoylacetone, benzoin, benzil and carvone.

³ Wheeler and Norton, THIS JOURNAL, 50, 2488 (1928).

⁴ Froom, Kapeller and Krauss, Ann., 447, 294 (1926).

3. 4-*p*-Tolythiosemicarbazide reacts readily with the above ketones to give easily purified solid derivatives having definite melting points.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF SWARTHMORE COLLEGE]
**THE INFLUENCE OF THE HALOGENS ON THE COLOR OF AZO
 DYES. THE SPECTRAL ABSORPTION OF CERTAIN
 MONO-AZO DYESTUFFS**

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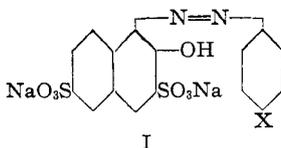
Introductory

Some years ago the author participated in one of a series of investigations on the relation of molecular structure to the color of azo dyes.¹ The influence of *o*-, *m*- and *p*-substitution of sulfur and oxygen was studied,^{2,3,4} and the preparation of dyes containing selenium is now under way.⁵

In all of this work color comparisons were made simply by the inspection of dyed samples. Recently the method of color analysis made possible by the development of the spectrophotometer has reached a stage where it is particularly valuable for this kind of study, and we hope that eventually all of the many dyes prepared in the investigations mentioned above may be quantitatively compared by means of this instrument.

This paper reports measurements of the spectra of dyes containing another group of the periodic system, the halogen family, with the spectrophotometer, to show the effect of *o*-, *m*- and *p*-substitution of chlorine, bromine and iodine. We attempted also to measure their absorption in the near ultraviolet with a quartz spectrograph and a densitometer, but because of the crudity of the apparatus were not able to obtain accurate results, and so have postponed this work until better instruments shall be available.

Preparation of the Dyes.—In order to preserve continuity with the dyes already studied, we selected dyes prepared by coupling an amine containing the halogen atom with R-salt. These compounds had the structure I, in which X is the halogen atom, shown here in the *p*-position. The *o*-, *m*- and *p*-chloro-, bromo- and iodo-anilines used were either bought on the market (Eastman Kodak Co.) or made by reduction of the corresponding halogeno nitrobenzene. In the latter case the amine was isolated as the hydrochloride.¹



¹ Foster and Reid, *THIS JOURNAL*, **46**, 1936 (1924).

² Waldron and Reid, *ibid.*, **45**, 2399 (1923).

³ Holt and Reid, *ibid.*, **46**, 2329; **46**, 2333 (1924).

⁴ Palmer and Reid, *ibid.*, **48**, 528 (1926).

⁵ See Foster and Brown, *ibid.*, **50**, 1182 (1928).