[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE FORCED REACTION BETWEEN ANILS AND PARA-THIOCRESOL. THE REDUCING ACTION OF THE MERCAPTO GROUPING

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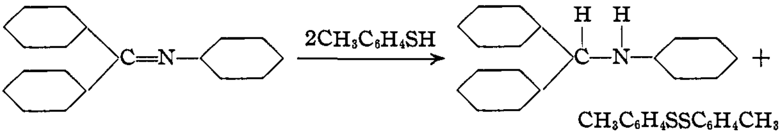
Introduction

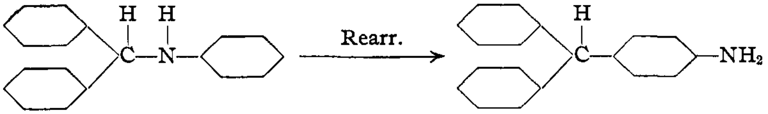
Recently, Gilman, Kirby and Kinney[1] described an unusual type of 1,4-addition to a conjugated system that is part aliphatic and part aromatic. This unique reaction which might have a significant bearing on the structure of benzene and the mechanism of substitution reactions of benzene certainly warranted confirmation with addenda other than organomagnesium halides. With this in mind, we selected *p*-thiocresol, $CH_3C_6H_4SH$, for another forced reaction study with benzophenone-anil because thiophenols lend themselves admirably as reagents for the characterization of conjugated systems.

In a preliminary experiment, in which a xylene solution of benzophenone-anil and *p*-thiocresol was refluxed for several hours, there was isolated a small quantity of di-*p*-tolyl disulfide, $CH_3C_6H_4SSC_6H_4CH_3$. Disulfides are formed by atmospheric oxidation of thiophenols; however, because the experiments were carried out in a trap[2] to exclude air, we concluded that the formation of di-*p*-tolyl disulfide was concomitant with reduction of the anil. This found support when the reaction products revealed *p*-thiocresol and di-*p*-tolyl disulfide equivalent to the initial quantity of *p*-thiocresol, and a basic compound free of sulfur, as well as some unaltered benzophenone-anil.

The basic product of reaction melted at 83–84° and it appeared altogether reasonable that it might be *p*-aminotriphenylmethane formed as a consequence of the reactions



$CH_3C_6H_4SSC_6H_4CH_3$ (II)



(III)

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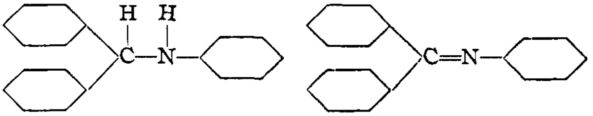
[1] Gilman, Kirby and Kinney, THIS JOURNAL, **51**, 2252 (1929). Kohler and Nygaard, *ibid.*, **52**, 4128 (1930), have just described a similar addition to the system $-CO-C_6H_5$.

[2] Gilman and Hewlett, *Rec. trav. chim.*, **48**, 1124 (1929).

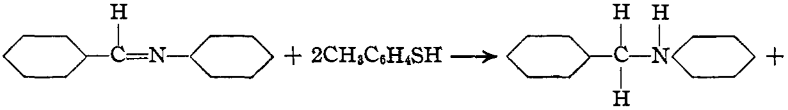
because Busch and Rinck[3] have shown that benzohydrylaniline (Reaction II) rearranges to *p*-aminotriphenylmethane when heated at an elevated temperature with aniline hydrochloride.

However, the compound was shown not to be the *p*-aminotriphenylmethane by comparison with an authentic specimen. It was subsequently established that Reaction II is correct, and that the benzohydrylaniline so formed united with a molecule of unaltered benzophenone-anil to give the complex



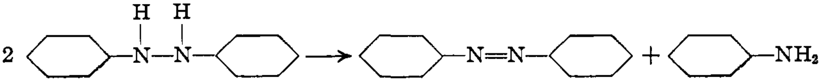
which melts at 83–84° and which is readily prepared by mixing equimolecular quantities of the two components in alcohol.[4]

The reduction of an anil is apparently a general reaction for this class of compounds inasmuch as benzalaniline was reduced rather smoothly under corresponding conditions to benzylaniline, as follows



$CH_3C_6H_4SSC_6H_4CH_3$ (IV)

Likewise, azobenzene was reduced to hydrazobenzene, but under our forced conditions the hydrazobenzene underwent the known[5] thermal decomposition to azobenzene and aniline



(V)

and in the presence of an excess of the reductant (*p*-thiocresol) the azobenzene was progressively converted to aniline. Of course, it is possible that a part of the azobenzene may have been reduced directly to aniline, but the isolation of some hydrazobenzene (as its rearrangement product, benzidine) indicates that the reduction to aniline probably proceeded in accordance with Reaction V.

There is, then, no question concerning the reducing action of *p*-thiocresol. However, it is only a mild reducing agent, as might have been predicted from the related hydrogen sulfide and alkaline sulfhydrates. Actually, it did not reduce, under our conditions, nitrobenzene or benzophenone. It is altogether reasonable to expect that a study of other mer-

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[3] Busch and Rinck, *Ber.*, **38**, 1761 (1905).

[4] Alessandri, *Gazz. chim. ital.*, **51**, 1, 75 (1921); *C. A.*, **15**, 2860 (1921).

[5] Hofmann, *Jahresber.*, p. 425 (1863); Biehringer and Busch, *Ber.*, **36**, 339 (1902); Stieglitz and Curme, *ibid.*, **46**, 911 (1913); Curme, THIS JOURNAL, **35**, 1143 (1913); Wieland, *Ann.*, **392**, 133 (1912); *Ber.*, **48**, 1098 (1915).

capto groups, alkyl as well as aryl, might reveal such compounds as useful, preferential, mild reductants.[6] However, this is beyond our immediate interests, which are concerned with the search of other addenda to support the unusual type of 1,4-addition shown by phenylmagnesium bromide.

We noted also that *p*-thiocresylmagnesium iodide, $CH_3C_6H_4SMgI$, did not react with either benzophenone-anil or benzalaniline in an ether–xylene solution. It was shown previously by Gilman and King[7] that this mercaptomagnesium halide underwent 1,4-addition with the ethylenic ketonic conjugated system in benzalacetophenone, $C_6H_5CH{=}CHCOC_6H_5$.

Experimental Part

Benzophenone-anil and *p*-Thiocresol.—In a typical experiment, 27.0 g. (0.105 mole) of benzophenone-anil[8] and 39.0 g. (0.315 mole) of *p*-thiocresol were dissolved in 200 cc. of xylene and refluxed for twenty-four hours in a flask connected with a trap[2] to exclude air. The cold reaction mixture was extracted with 10% sodium hydroxide to remove 13 g. or 33.3% of the thiocresol. Then the resulting mixture was concentrated under reduced pressure to remove the xylene, and the resulting oil was extracted with petroleum ether (b. p. 40–60°) and filtered. The molecular complex of benzohydrylaniline and benzophenone-anil is but slightly soluble in petroleum ether. By this treatment 15 g. or a 58% yield of the benzohydrylaniline and benzophenone-anil complex was isolated and identified by a mixed melting point determination.

The oily residue from the petroleum ether yielded 10 g. or 37% of benzohydrylaniline. This was converted to its hydrochloride, which was identified by a mixed melting point determination with an authentic specimen prepared in accordance with the directions of Busch.[9] The isolation of the benzohydrylaniline indicates that the complex with benzophenone-anil is first formed and then undergoes reduction.

Other products recovered were 22.1 g. or 56.6% of di-*p*-tolyl disulfide and a trace of aniline. Like products were obtained in another experiment when a small quantity of piperidine was used as a catalyst.

Benzalaniline and *p*-Thiocresol.—In one experiment 25.5 g. (0.141 mole) of benzalaniline[10] and 69.4 g. (0.564 mole) of *p*-thiocresol in 200 cc. of xylene were refluxed for twenty-six hours. The products obtained were 36 g. or 50.2% of *p*-thiocresol, 32 g. of di-*p*-tolyl disulfide (equivalent to 45.7% of *p*-thiocresol) and 19.4 g. of benzylaniline. All of the benzylaniline was not recovered, because of the difficulty of effecting a complete separation from traces of aniline and some unaltered benzalaniline. The identity of benzylaniline was confirmed by mixed melting point determinations of the hydrochloride and oxalate prepared from it, with authentic specimens of these salts.

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[6] Possibly such reduction of organic compounds by organo-mercapto groups may have been noted by others. We are unfamiliar with such studies.

[7] Gilman and King, THIS JOURNAL, **47**, 1136 (1925).

[8] The benzophenone-anil was prepared in accordance with the direction of Reddelien, *Ber.*, **42**, 4759 (1909). Unfortunately, the yields so obtained in several preparations were only about 20%. Single preparations were also made after the modifications of Reddelien, *Ber.*, **48**, 1462 (1915), and of Knoevenagel, *J. prakt. Chem.*, [2] **89**, 37 (1913), and again with yields distinctly below those reported. Possibly the difficulty lies in varying purities of the condensing agents.

[9] Busch, *Ber.*, **37**, 2691 (1904); Busch and Rinck, *Ber.*, **38**, 1769 (1905).

[10] Prepared in accordance with the directions given in "Organic Syntheses," John Wiley and Sons, Inc., New York, **1928**, Vol. VIII, p. 22.

The same products were obtained in another experiment in which 0.5 cc. of piperidine was used as a catalyst.

Azobenzene and *p*-Thiocresol.—A solution of 18.2 g. (0.1 mole) of azobenzene and 37.2 g. (0.3 mole) of *p*-thiocresol in 200 cc. of xylene was refluxed for twenty-five hours. As in all other experiments, a trap[2] was used to exclude air. The products obtained were 9.5 g. of aniline, 0.1 g. of benzidine (from a sulfuric acid treatment of the hydrazobenzene present), 5.5 g. of *p*-thiocresol and 90% of the di-*p*-tolyl disulfide which should have formed on the basis of the reduction products isolated.

Miscellaneous.—After heating 0.075 mole of benzophenone-anil with four molecular equivalents of *p*-thiocresylmagnesium iodide in an ether–xylene solution at 103–107° for twelve hours, 96% of the anil was recovered. In addition, 0.3 g. of aniline was isolated. Another experiment under corresponding conditions yielded a 95% recovery of the anil, and traces of aniline and di-*p*-tolyl disulfide.

Subsequent to refluxing three equivalents of *p*-thiocresylmagnesium iodide with benzalaniline in an ether–xylene solution at 114–124° for forty hours, 96% of the *p*-thiocresol was recovered.

The recovery of *p*-thiocresol in an experiment in which four molecular equivalents of it were refluxed with benzophenone in xylene for twenty-six hours was 97.8%. A like recovery of *p*-thiocresol was had in an experiment wherein eight equivalents were heated with nitrobenzene in xylene for twenty-six hours.

Summary

In continuation of studies on the unique 1,4-addition to a conjugated system which is part aliphatic and part aromatic, benzophenone-anil and benzalaniline, respectively, were heated with *p*-thiocresol. No 1,4-addition was observed. Instead the thiocresol acted as a reducing agent, and was converted to di-*p*-tolyl disulfide. It also reduces azobenzene, but not nitrobenzene or benzophenone. *p*-Thiocresylmagnesium iodide did not react with the anils.

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THE CHLORINE DERIVATIVES OF VANILLIN AND SOME OF THEIR REACTIONS

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In previous work in this Laboratory[1] the bromine substitution products of vanillin were studied for the purpose of completing the list and to obtain derivatives with which to test further the observations of Brady and Dunn,[2] who found that "no evidence of the existence of a second isomeride has been obtained in the cases of any hydroxybenzaldoximes," but that "certain negative substituents in the benzene ring seem to favor the existence of two isomeric oximes." Since stereoisomers were not obtained from

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[1] Raiford and Hilman, THIS JOURNAL, **49**, 1077, 1571 (1927); Raiford and Stoesser, **50**, 2556 (1928).

[2] Brady and Dunn, *J. Chem. Soc.*, **105**, 825 (1914); **107**, 1859 (1915).