XXII.—ON THE SUBSTITUTED TOLYL COMPOUNDS.

BY JAS. H. STEBBINS, JR., B.S.

In 1875, C. L. Jackson and Woodbury Lowry published an article in the *Berichte d. d. chem. Gesell.* (1875, 1672), entitled, "On Substituted Benzyl Compounds," and including the following substances:

Parabrombenzyl bromide, C_6H_4Br—CH_2Br. This substance was prepared according to the process indicated by Neuhof (Zeitschr. f. Chem., 1866, 653), for the preparation of chlorbenzyl chloride, namely, by passing bromine vapor into the vapor of boiling parabromtoluole. The boiling point rose, while the bromine vapors were being passed in, and copious fumes of hydrobromic acid were evolved. On cooling, the liquid crystallized into one solid mass, which, after being crystallized from boiling alcohol, showed a constant melting point. It crystallizes from alcohol easily, in long, white needles.

The brown, oily liquid accompanying these (probably a mixture of parabromtoluole and orthobrombenzyl bromide), crystallizes by slow evaporation, in large quadratic prisms. This substance possesses a pleasant aromatic odor, but the vapor irritates the eyes, and mucous membrane of the nose and mouth. It may be distilled with steam, but only very slowly. It sublimes easily, and burns with a green tinged, sooty flame. Insoluble in water, but pretty soluble in cold, and very soluble in warm alcohol. It is also soluble in ether, CS_2, $HC_2H_3O_2$ and toluole.

If heated with one molecule of $NaC_2H_3O_2$ and absolute alcohol, in a flask connected with a reflux condenser, sodium bromide is precipitated out, and a thick liquid is obtained, possessing a pleasant odor. If this substance be heated with CuO, it will burn with a green flame. This body was, therefore, looked upon as a brombenzylacetate.

Metabromtoluole, prepared according to Wroblewskey's method (Ann. Chem. Pharm., 168, 153), on being treated with bromine vapor, yielded likewise a liquid, the smell of which differed considerably from that of the preceding substance, but it attacked the eyes and nose in the same way. Treated with $NaC_2H_3O_2$ and absolute alcohol, a bromoacetate was likewise obtained.

The orthobromtoluole, treated in the same way, yielded orthobrombenzyl bromide.

In 1877, C. L. Jackson and Woodbury Lowry (Ber. d. d. chem. Gesell., 1877, 1209) published their second paper, entitled, "On Parabrombenzyl Compounds," and add that parabrombenzyl bromide

may likewise be prepared by treating benzyl bromide, in the cold, with bromine and a little iodine ; but they found that this method is far inferior to the one at first described.   Farther on they describe a few more compounds, obtained from parabrombenzyl bromide, which I will now repeat, as I shall, later on, have occasion to refer to them.

Parabrombenzyl alcohol, $C_6H_4Br—CH_2OH$. This was prepared by heating. parabrombenzyl bromide for several days (in a flask connected with a reflux cooler), with water, until the eyes were no longer attacked.   It was also prepared from parabrombenzylacetate, by heating to 150°, with aqueous ammonia.   The alcohol appears as long, flat and elastic needles, with pearly lustre and disagreeable odor —melting point, 69°—and may be distilled in a current of steam.

Parabrombenzyl cyanide, $C_6H_4BrCH_2.CN$, was prepared by boiling parabrombenzyl bromide with an alcoholic solution of KCN.

Parabromalphatoluylic acid, $C_6H_4BrCH_2COOH$, was prepared from the foregoing, by heating it in sealed tubes, with hydrochloric acid, to 100°.

Alcoholic ammonia acts readily on parabrombenzyl bromide, at the ordinary temperature, forming a crystalline mass, which is nearly insoluble in alcohol.   This mass consists of two substances, one crystallizing in leaflets, and the other in needles.   The latter showed itself to be triparabrombenzylamine, $(C_6H_4BrCH_2)_3N$.

These compounds seemed to be of so interesting a nature, that I had for some time contemplated the idea of working on them ; but for fear of infringing on Prof. Jackson's work, the idea was dropped, until recently, when I determined to experiment on the substituted tolyl compounds, which seemed to offer a large and unexplored field to work upon.

As xylole is the next higher homolgue to toluole, it seemed but natural that I might reproduce all of the compounds detailed in the beginning of this paper, with the difference of containing the tolyl, instead of the benzyl radical.   With this point in view, I proceeded as follows :

I first prepared my bromxylole, by treating one mol. of commercial xylole (surrounded with cold water), with four atoms of bromine, which were allowed to flow in drop by drop.

During the operation, copious fumes of HBr were evolved, and the oily liquid was then washed with water made alkaline with KOH, so as to absorb all traces of HBr and Br.

It was then thoroughly washed with distilled water, and, after being mixed with a few pieces of $CaCl_2$, placed under the air pump to dry.

The oil thus obtained, when perfectly dry, is clear, and possesses a light yellow color. It boils at 197°.25, instead of 204°, which is the boiling point for metabromxylole, thus showing that it is a mixture of the meta and parabromxylole, the former predominating. The reaction here taking place, may be expressed as follows :

$$C_6H_4(CH_3)_2 + 2Br_2 = C_6H_3Br(CH_3)_2 + HBr.$$
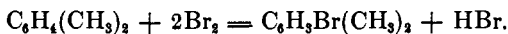
Action of bromine on metabromxylole.—There are two methods of bromizing; one, already indicated by Jackson, by passing a stream of bromine vapor into the vapors of boiling metabromxylole; and the other, by allowing a small stream of bromine to fall gradually into metabromxylole, heated from 135–140°. This method was also tried by Jackson and Field, with far better results than with the previous one.

The proportions used were respectively, 10.3 grms metabromxylole and 17.7 grms bromine. The two substances were mixed, as already stated, and heated in an oil bath, from 135–140°. The heating lasted about four hours, and, during this time, copious fumes of HBr were given off, thus showing that the substitution in the side chains was taking place freely.

The result was a black, thick oil, with a strong odor resembling parabrombenzyl bromide, and likewise attacking the eyes and nose, though not so strongly as the latter.

It was poured on a large watch glass to cool, and placed under the air pump, in the hope that by so doing it would crystallize ; but several days standing produced no result. It was therefore supposed that the substance was not pure, but might be a mixture of the para and meta combinations, and that by submitting the raw material to distillation in a current of steam, the more volatile of the two combinations would distill over, while the less volatile would remain behind. This supposition was fully verified, for, no sooner had steam begun to pass through the solution freely, than a clear, light colored oil began to distill over. The distillation is slow, and it was some time before all the oil had passed over. This light colored oil has a pleasant, aromatic odor, and attacks the eyes and nose very strongly. It is easily soluble in hot alcohol, but, on cooling, separates out in oil drops again.

This oil is probably the metabromtolyl bromide, and, as the corresponding metabrombenzyl bromide is a white crystalline body, it seemed strange that it should not crystallize. After trying several methods to obtain it in a crystalline state, without success, I became discouraged, and placed the oil away under the air pump for several

days.   When I again looked at the oil I was greatly surprised, for it was filled with pretty little white crystals, showing that the oil only required time to crystallize.

The black oil remaining in the distilling apparatus is probably the parabromtolyl bromide, which I have not yet had occasion to examine.

The reaction taking place here, may, I think, be expressed in the following equation :

$$C_6H_3Br(CH_3)_2 + 2Br_2 = C_6H_3Br\!\!\begin{array}{l}CH_2.Br\\CH_2.Br\end{array}\!\! + 2HBr.$$
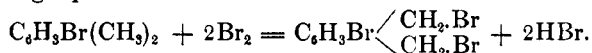
I have not had time to investigate this substance more extensively, but I propose next fall to include among my experiments all of Jackson's compounds, and study each one individually.

In 1879 (Ber. d. d. chem. Gesell., 1965), Jackson and White published an article describing the synthesis of anthracene, by acting on orthobrombenzyl bromide with metallic sodium.

In carrying out their experiments, they treated a dilute solution of orthobrombenzyl bromide, in ether, with small pieces of sodium, and heated gently.   A violent reaction took place, and in a short time the smell of the orthobrombenzyl bromide disappeared.   The mixture thus obtained, was distilled with water, the distillate separating into three layers.   The substance collected in the distilling tube, has a strong smell of anthracene, and was found to be bihydrated anthracene, which, upon being treated with strong H_2SO_4, in the water-bath, yielded pure anthracene, melting at $213°$.

This demonstrates that the two C atoms in anthracene, stand in relation to the two benzole nuclei, in the 1 : 2 position.

The formation of anthracene may be represented as follows, whereby it will be seen that two mols. of orthobrombenzyl bromide unite with one another, giving off HBr, viz.:
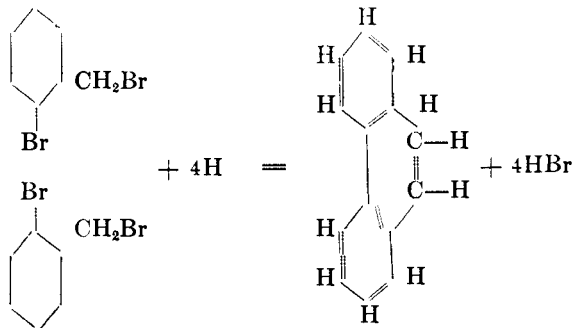
In the same way, I hope to arrive ·at the constitution of pyrene, which is $C_{16}H_{10}$, only, in this case, I am not certain what position the carbon atoms hold, and will, therefore, have to try all the three brom-tolyl bromides. If we combine two molecules of, say, metabromtolyl bromide, and treat the mixture with sodium, we should get a bihydrated pyrene, and this, treated with H_2SO_4, should yield pure pyrene.

XXIII.—On a New Sulpho Acid of Phenanthrene.

By Henry Morton and William E. Geyer.

A monosulpho acid of phenanthrene was first prepared by Graebe,[*] and subsequently by Rehs.[†] Graebe heats phenanthrene with its own weight of oil of vitriol, for some time, on the water-bath. Rehs uses slightly fuming acid, apparently at ordinary temperatures·

Merz and Weith [‡] have shown that when naphthalene is heated with sulphuric acid, at 100°, α-naphthalene sulpho acid is the main product, but if the temperature is raised to 160–170°, the β modification is almost exclusively formed. We have found that in the same way, phenanthrene, also, forms two distinct monosulpho acids. That formed according to Graebe's method, we propose to call the α-acid, ours the β-naphthalene sulpho acid.

To serve as a means of comparison, we first prepared the α-acid. The process is simple, but the yield is small, the greater part of the phenanthrene remaining unattacked. To prepare the β-acid, three parts of phenanthrene were heated with two parts of sulphuric acid, in a paraffine bath, to 170°, for three hours. Towards the end, the temperature was, for a short time, raised to 190°. Much vapor of water and sulphurous acid were given off, during the entire time of heating. On cooling, there was obtained a very black, tenacious pitch. This, with the exception of a little unaltered phenanthrene, dissolves in water to a very dark greenish-black liquid. When this liquid is much diluted, heated to boiling, and neutralized with lead carbonate, the black coloring matter is completely carried down with

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* Ann Chem. u. Pharm., **167**, 152.

† Ber. d. d. chem. Gesell., **10**, 1252.

‡ Ber. d. d. chem. Gesell., **3**, 195.