

number of isomers of  $C_{19}H_{40}$  was found to be in error, and the correct value is here given. As in the case of the alcohols, the numbers of structurally isomeric hydrocarbons also form an approximate geometric progression. Here again the inverse ratios of successive numbers are always slightly increasing, and have decreasing first differences. The extrapolated average inverse ratio of consecutive numbers over the carbon content interval from 60 to 70 is 2.72, and hence the value for  $C_{70}H_{142}$  is approximately  $4.91 \times 10^{26}$ .

Several corrections are to be noted in the original papers by Henze and Blair. On line 2, p. 3045, for " $(n-1)6$  an integer," read  $(n-1)/6$  an integer. In the discussion of the number of hydrocarbons of even carbon content of group A, p. 3080, line 19, the factor  $1/2$  should be inserted to make the formula read correctly. This remark also applies to the formula for hydrocarbons of odd carbon content resulting from joining alkyls of  $(N+1)/2$  and  $(N-1)/2$  carbon atoms through an intermediate carbon atom, p. 3080, line 36. In group B, type b, Case 2, page 3082, line 23, it might be well to mention explicitly that  $j$  and  $k$  cannot interchange values, which may be expressed by requiring that  $j$  always exceed  $k$ . For completeness, it may be added that in the formula for compounds of odd carbon content of Group A, it is implied that the definition of  $T_0$  is unity. These corrections apply to the references noted, but were correctly applied in the computations of the authors.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE BAKELITE CORPORATION]

## MOLECULAR REARRANGEMENT IN THE HYDROLYSIS OF CHLOROTOLUENES WITH ALKALI

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It is known that molecular rearrangement takes place when ortho or para chlorobenzene sulfonic acid is fused with potash, both compounds yielding resorcinol by this treatment.<sup>1</sup> It now appears that such a rearrangement may be general with halogen substituted benzenes carrying aliphatic side chains. We have carried out a number of experiments on the hydrolysis of substituted chlorobenzenes carrying normal aliphatic side chains and have been singularly unsuccessful in obtaining pure products. This was particularly apparent in the case of the products obtained from the hydrolysis of ortho and para chloro substituted derivatives of ethylbenzene, normal butylbenzene, and normal amylbenzene. These compounds are not adequately described in the literature and the phenols derived from them have been described<sup>2</sup> but there are no quantitative methods for purifying

<sup>1</sup> Beilstein, 4th ed., Vol. VI, p. 796.

<sup>2</sup> Coulthard, Marshall and Pyman, *J. Chem. Soc.*, 280 (1930).

them in the presence of their isomers. The para substituted phenols in general have higher melting points than the corresponding ortho and meta derivatives but usually are very close to the meta derivatives in boiling point and many other properties. The fact that in some cases where we expected to obtain the para compounds the product, when purified by careful fractional distillation, distilled at almost exactly the correct point and yet failed to crystallize on cooling led us to believe that the meta isomer might be present as an impurity. A comparison of the properties of the product derived from *p*-ethylchlorobenzene with a sample of *p*-ethylphenol from another source seemed to confirm this explanation.

As a final check on the above we have carried out the hydrolysis of *o*- and *p*-chlorotoluenes in sodium hydroxide at temperatures above 300° and found *m*-cresol to be present in the product from each. The hydrolyses were carried out in a manner similar to that used by Meyer and Bergius<sup>3</sup> for the hydrolysis of chlorobenzene. These authors state that *p*-cresol is easily obtained from chlorotoluene, but do not state which chlorotoluene. In our experiments the purified phenolic portion from the *o*-chlorotoluene showed a *m*-cresol content of 25.3% and that from the para 38.2%. There was some slight evidence that all three cresols were present in each case but our method of analysis was not sufficiently accurate to detect small amounts of ortho and para. A slightly modified Raschig nitration method<sup>4</sup> was used for the meta determinations. This has been checked thoroughly in this and other laboratories and can be relied upon with certainty to give results accurate to 2% of the true value under our conditions.

### Experimental

**Hydrolysis of Chlorotoluenes.**—The autoclave was 61 cm. long by 7 cm. inside diameter, and was fitted with a thermocouple well and flexible connections to a pressure gage and relief valve. It was made of carbon steel and the capacity was about 2.2 liters. It was heated electrically and was mounted on a shaking machine. The *o*- and *p*-chlorotoluenes used were obtained from the Eastman Kodak Company and were not given any further purification before use. The para compound had a freezing point of 7.1°. The melting point is given in the literature as 6.5–7.5°.

One hundred twenty-six grams (one mole) of *o*-chlorotoluene, 1332 g. (5 moles) of 15% sodium hydroxide, and 10 g. of freshly reduced copper powder were heated together for two hours at 315–320°. The shaking machine was run intermittently (five minutes on, ten minutes off). About two hours was required to raise the reaction mixture to the required temperature and a somewhat longer time for it to cool. When cold the contents were removed from the autoclave and extracted with ether. The water layer was then acidified and again extracted. The yield of crude alkali-soluble material was 60 g. *p*-Chlorotoluene treated in the same manner yielded 63 g. of crude product.

The greater part of the products from each of the runs described above was fractionated through a column of good efficiency built to handle small amounts of material. The data from the distillations and analyses were:

<sup>3</sup> Meyer and Bergius, *Ber.*, **47**, 3155 (1914).

<sup>4</sup> *Z. angew. Chem.*, **31**, 759 (1900).

	From <i>o</i> -chlorotoluene	From <i>p</i> -chlorotoluene
Still charge	32.9 g.	40.0 g.
Fraction 197-202°	9.7 g.	26.8 g.
Fraction 202-235°	0.4 g.	0.5 g.
Total distillate 182-235°	25.9 g.	30.2 g.
Meta cresol in 197-202° cut	67.5%	43.1%

When these results are calculated back to the total crude yields (parts of which were used for another purpose) we find that *o*-chlorotoluene yielded 55.4% of pure mixed phenols, calculated as cresol, and 25.3% of this material was *m*-cresol. The corresponding figures for *p*-chlorotoluene are 55.5 and 38.2%. No trace of phenol was found in either product.

**Preparation and Hydrolysis of Ethylchlorobenzenes.**—The products obtained from the chlorination of ethylbenzene were carefully fractionated and two fractions separated, one boiling chiefly at 180°, the other at 185°. Tohl and Eberhard<sup>5</sup> give the boiling point for *p*-ethylchlorobenzene as 180–182°. The fraction boiling at 180° yielded on oxidation with alkaline permanganate an acid which melted at 130–132°. *o*-Chlorobenzoic melts at 137°. The meta and para acids both melt much higher so the material boiling at 180° is *o*-ethylchlorobenzene. Both fractions were hydrolyzed in a manner similar to that used for the chlorotoluenes and the products purified in the same manner. Since the higher boiling fraction was not identified and might therefore contain some of the meta compound, its hydrolysis products will not be discussed at length. That which was obtained from several runs on the ortho was combined before purification and on distillation, cuts were taken as follows: 168–205°, 20.7 g.; 205–211° (205°), 45.5 g.; 211–218°, 7.8 g.; 218–222° (219°), 112.2 g.; 222–245°, 5.2 g. The total still charge was 224.5 g. Temperatures in parentheses are points at which the larger portions distilled. Boiling points given in the literature for ethylphenols are:<sup>6</sup> ortho, 206.5–207°; meta, 217°; and para, 218°. The lower boiling constituent is undoubtedly the ortho compound and the fraction boiling at 218–222° is probably a mixture of meta and para with meta largely in excess. It did not crystallize when seeded with crystalline *p*-ethylphenol from another source. The refractive index ( $n_D$ ) was 1.5294 at 25°; *p*-ethyl gives 1.5288 for the supercooled liquid. A phenylurethan was prepared by the method of Fromm and Eckard<sup>7</sup> and it melted at 133–137°. The phenylurethan from *p*-ethylphenol melts at 120° and that from the meta at 138.8°.<sup>8</sup>

### Summary

Ortho and para chlorotoluenes when hydrolyzed with sodium hydroxide undergo partial molecular rearrangement, yielding a mixture of products containing *m*-cresol.

Results on the hydrolysis of *o*-ethylchlorobenzene indicate that the rearrangement is general.

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<sup>5</sup> Beilstein, 4th ed., Vol. V, p. 354.

<sup>6</sup> Beilstein, 4th ed., Vol. VI, pp. 471–472.

<sup>7</sup> Eckard, *Ber.*, **56**, 948 (1923).

<sup>8</sup> Steinkopf and Höpner, *J. prakt. Chem.*, [2] **113**, 137 (1926).