Reaction of IV with Phosphorus Trichloride. Attempted Preparation of α-Cyclopropylbenzyl Chloride.—The carbinol (5.6 g.) was dissolved in 50 cc. of dry ether and cooled in Dry Ice–alcohol. The solution was stirred during the dropwise addition of 2.6 g. of phosphorus trichloride in 10 cc. of dry ether. The solution was stirred for 1 hr. in the cold; the bath was then removed and the mixture was allowed to stand 2 hr.

Water was added and the layers were separated. The organic layer was washed with sodium bicarbonate solution and dried over Drierite. The product boiled over a wide range (120–140° at 16 mm.), and there was an appreciable amount of non-volatile residue. Through redistillation a small amount of liquid boiling at 135° (19 mm.), $n^{25}D$ 1.5620, was obtained. The infrared spectrum indicated that the substance isolated was crude IX.

α-Cyclopropylbenzylamine (VI). A. By Catalytic Reduction.—Cyclopropyl phenyl ketoxime (16.1 g., 0.1 mole) was dissolved in 200 cc. of absolute alcohol containing 0.25 mole of dry hydrogen chloride. Hydrogenation was carried out with 2.0 g. of 5% palladium on charcoal at a pressure of 30 lb. In 2 hr., the mixture was filtered; the filtrate was concentrated to about 50 cc. and diluted with dry ether. Twelve grams (65%) of product, m.p. 237–238°,[21] was obtained.

B. By Reduction with Lithium Aluminum Hydride.—The oxime (30 g., 0.19 mole) was dissolved in 150 cc. of dry ether and added dropwise to 14.1 g. (0.37 mole) of the hydride in 150 cc. of dry ether. The mixture was refluxed for two days.

The product was processed in the usual way. Distillation yielded 22.8 g., b.p. 103–115°, $n^{25}D$ 1.5390–1.5492. Since the product was obviously a mixture, it was combined with similar material from an earlier run (total, 32 g.) and dissolved in a slight excess of dilute hydrochloric acid. The solution was extracted with ether to remove any neutral substance, and then it was neutralized to a methyl red end-point. The oil which separated was extracted with ether (solution A). The aqueous solution was now made basic and again extracted with ether (solution B).

Both solutions were dried over potassium hydroxide and treated with dry hydrogen chloride. Solution B yielded 25.9 g. of the hydrochloride of VI, m.p. 224–226°. The melting point was raised to 233–234° by recrystallization from ethanol–ether. Solution A yielded 10.0 g., m.p. 173–176°. Several recrystallizations from alcohol did not change the melting point. From a consideration of the weakly basic character of the amine and the analogous rearrangements observed by others,[10,11] the substance is assigned the structure of N-(cyclopropylmethyl)-aniline hydrochloride (X·HCl).

Anal. Calcd. for $C_{10}H_{13}N{\cdot}HCl$: C, 65.4; H, 7.7; N, 7.6. Found: C, 65.5; H, 7.8; N, 7.7.

(α-Cyclopropylbenzyl)-urea.—The amine hydrochloride (9.2 g., 0.05 mole) was dissolved in 40 cc. of water and treated with 4.9 g. (0.06 mole) of potassium cyanate in 20 cc. of water. After several hours, the product was separated by filtration; the yield was 8.0 g. (85%), m.p. 143–146°. An analytical sample prepared from alcohol melted at 145–146°.

Anal. Calcd. for $C_{11}H_{14}N_2O$: N, 14.7. Found: N, 14.9.

Methyl N-(α-Cyclopropylbenzyl)-carbamate.—A Schotten–Baumann reaction was carried out with 18.4 g. of VI hydrochloride and 14.3 g. of methyl chloroformate. Filtration yielded 16.2 g. (79%), m.p. 88–90°.

Recrystallization from dilute alcohol gave an analytical sample melting at 88–90°.

Anal. Calcd. for $C_{12}H_{15}NO_2$: N, 6.8. Found: N, 6.8.

Benzylcyclopropane (VII).—The ketone III (29.2 g., 0.2 mole), 24 g. (0.4 mole) of 85% hydrazine hydrate, 26.4 g. (0.4 mole) of 85% potassium hydroxide and 150 cc. of diethylene glycol were refluxed in an oil-bath at 120° for 1 hr. The condenser was then set for distillation and the temperature was gradually raised to 200°. The product steam distilled during this time. After 1 hr. at 200°, the reaction mixture was cooled somewhat and treated with 20 cc. of water. The steam distillation was then continued for an additional hour.

The oil was separated from the water by means of ether. The dried ether layer was concentrated and distilled, yielding 22 g. (83%), b.p. 188°, $n^{25}D$ 1.5140. A portion was redistilled over sodium for analysis; all came over at 83–84° (20 mm.), $n^{25}D$ 1.5130.

Anal. Calcd. for $C_{10}H_{12}$: C, 90.9; H, 9.2. Found: C, 90.9; H, 9.2.

NORTH CHICAGO, ILLINOIS

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(21) N. Kizhner, *J. Russ. Phys. Chem. Soc.*, **43**, 1163 (1911) [*C. A.*, **6**, 597 (1912)], reported m.p. 220–221°.

[CONTRIBUTION NO. 2131 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Mechanisms for Liquid Phase Hydrolyses of Chlorobenzene and Halotoluenes[1]

BY ALBERT T. BOTTINI[2] AND JOHN D. ROBERTS

RECEIVED SEPTEMBER 4, 1956

A study of the rearrangements which occur during the high temperature liquid phase hydrolyses of the halotoluenes has shown that the extent of rearrangement is a sensitive function of temperature, base strength and the nature of the halogen. These hydrolyses involve either a benzyne (elimination–addition) mechanism, which gives both rearranged and unrearranged products, or an SN2-type mechanism. The SN2-type mechanism was found to be favored at lower temperatures, in the presence of weaker bases and with the more easily ionizable halogens. By suitable choice of conditions, one or the other reaction could be made to occur almost exclusively. Chlorobenzene-1-^{14}C, with 4 *M* sodium hydroxide solution at 340°, gave 58 ± 1% phenol-1-^{14}C and 42 ± 1% phenol-2-^{14}C, which indicates that under these conditions the benzyne mechanism predominates but is not the exclusive reaction path.

It has been known for many years that the individual chlorotoluenes are hydrolyzed with sodium hydroxide solution at temperatures above 300° to yield mixtures of cresols.[3,4] The extent and character of these rearrangements bear a marked similarity to what would be expected if a "benzyne" (elimination–addition) mechanism[5] were operative. Thus, the entering hydroxyl group has never been found farther than one carbon away from the leaving chlorine, and the chlorotoluenes and cresols (as sodium cresolates) are apparently not isomerized

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(1) Presented in part at the National Academy of Science Meeting in Pasadena, California, November 4, 1955; J. D. Roberts, A. T. Bottini and D. A. Semenow, *Science*, **122**, 881 (1955).

(2) National Science Foundation Predoctoral Fellow, 1954–1957.

(3) V. E. Meharg and I. Allen, Jr., THIS JOURNAL, **54**, 2920 (1932).

(4) R. N. Shreve and C. J. Marsel, *Ind. Eng. Chem.*, **38**, 254 (1946).

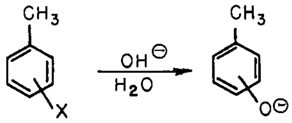
(5) (a) J. D. Roberts, H. E. Simmons, Jr., L. A. Carlsmith and C. W. Vaughan, THIS JOURNAL, **75**, 3290 (1953); (b) J. D. Roberts, D. A. Semenow, H. E. Simmons, Jr., and L. A. Carlsmith, *ibid.*, **78**, 601 (1956); (c) J. D. Roberts, C. W. Vaughan, L. A. Carlsmith and D. A. Semenow, *ibid.*, **78**, 611 (1956).

under the reaction conditions.[6,7] In the present research, it has been found that the compositions of the cresol mixtures obtained from hydrolyses of the halotoluenes under various conditions are best understood in terms of concurrent operation of the benzyne mechanism and a non-rearranging SN2-type mechanism. The proportion of reaction proceeding by either path is easily correlated with the factors which govern the ratio of elimination (E2) to direct substitution (SN2) in reactions of alkyl halides. As expected, direct substitution is favored at lower temperatures, with weaker bases and with the more easily ionizable halogens, *i.e.*, I>Br>Cl. Some indication has been obtained that a non-rearranging displacement is catalyzed by a manganese steel surface at lower temperatures, and that use of potassium hydroxide in place of sodium hydroxide increases the amount of rearrangement at lower temperatures. These last two findings were not thoroughly investigated.

Earlier research with chlorobenzene[8,9] and chlorotoluenes[4] indicates 4 *M* sodium hydroxide solution to be the optimum medium for aryl halide hydrolyses. Most of our results were obtained with this medium although a number of experiments were conducted with 1–8 *M* sodium hydroxide solution. The hydrolysis yields were found to vary considerably with hydroxide concentration but no significant differences in product composition were observed over the range of concentrations employed, provided the conditions were otherwise identical. Approximately 20 g. of halotoluene and 250 ml. of sodium hydroxide solution were heated to the desired temperature in 1.5–2.5 hours, shaken for two hours and allowed to cool. The reaction mixtures were shaken only at the reaction temperature. Usually the reactions were conducted in a monel liner enclosed in a manganese steel bomb. The resulting cresols were isolated, purified by distillation and analyzed by means of their infrared spectra. The results are presented in Table I. The cresol analyses are considered to be accurate to ± 1–2%, since no deviations greater than this were observed when known cresol mixtures were carried through the isolation procedure. However, since the results of five runs similar to those in Table I showed differences in product composition as large as ±4%, no greater accuracy than this is claimed for the reaction product compositions. The figures for % conversion to cresols may be taken as a rough indication of the reaction rate within the limitations imposed by the fact that the reaction times were not exactly the same, variations were noted in the extent of formation of secondary products and in all cases heterogeneous mixtures were employed.

TABLE I

ORIENTATIONS IN HYDROLYSES OF HALOTOLUENES WITH SODIUM HYDROXIDE SOLUTIONS[a]



X[b]	Temp.,[c] °C.	NaOH, *M*[d]	Conversion,[e] %	Product composition[f] *Ortho*, %	*Meta*, %	*Para*, %
o-Cl[g]	340	4	68	48.2	51.8	..
m-Cl	300	4	25	18.0	68.0	14.0
m-Cl[h,i]	300	4	27	18.4	69.0	12.6
m-Cl	340	4	56	21.4	63.6	15.0
p-Cl[h,i]	250	1	3.6	..	9	91
p-Cl[h]	250	4	1.2	..	14.4	85.6
p-Cl[j]	250	4	~0.3	..	~40–50	~50–60
p-Cl	300	4	17	..	47.7	52.3
p-Cl	340	1	23	..	48.6	51.4
p-Cl	340	2	39	..	49.3	50.7
p-Cl	340	4	59	..	50.4	49.6
p-Cl	340	8	50	..	50.0	50.0
p-Cl[k]	360	4	54	..	50.0	50.0
o-Br	250	4	15	53.6	47.4	..
o-Br	340	4	63	45.4	54.6	..
m-Br	250	4	15	12.6	79.8	7.6
m-Br	340	4	60	23.9	60.2	15.9
p-Br	250	1	26	..	21.5	78.5
p-Br	250	4	17	..	25.8	74.2
p-Br	340	1	38	..	50.0	50.0
p-Br	340	4	55	..	54.6	45.4
o-I	250	4	22	63.4	36.6	..
o-I	340	4	50	41.7	58.3	..
m-I	250	4	38	5.7	88.9	5.4
m-I	340	4	47	19.8	66.1	14.1
p-I	250	1	45	..	<3	~97
p-I	250	4	45	..	<3	~97
p-I	340	1	44	..	49.2	50.8
p-I	340	4	43	..	48.7	51.3

[a] Unless otherwise stated, all reactions were carried out in a monel liner in a manganese steel bomb for 2 hours. [b] Approximately 20 g. [c] Deviations are ±4° at 250° and 300° and ±5° at 340° and 360°. [d] In all cases, 250 ml. [e] Percentage of halide converted to cresols, not corrected for recovered starting material. [f] Better than ±4%. [g] This result may be several per cent. in error. E. C. Britton, U. S. Patent 1,996,744, *Chem. Zentr.*, **106**, II, 1962 (1935), reported that 59% *m*-cresol is formed from *o*-chlorotoluene on hydrolysis with sodium hydroxide solution. [h] No liner was used. [i] Reaction time was 6 hours. [j] Two runs of 2.5 and 6 hours. The products were contaminated with phenol. [k] Reaction time was 0.5 hour.

The cresol mixtures obtained from the hydrolyses of *p*-halotoluenes were spectrophotometrically free of *o*-cresol. Furthermore, no *p*-cresol was detected in hydrolyses of *o*-halotoluenes. These results establish that the cresols (as cresolate ions) and halotoluenes are not isomerized under the reaction conditions. At 340°, the various *o*-halotoluenes gave essentially identical mixtures of *o*- and *m*-cresols. The *p*-halotoluenes behaved similarly and gave essentially identical mixtures of *m*- and *p*-cresols. These results are easily accounted for by the benzyne mechanism.[10] Thus, the *o*- and *p*-

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(6) R. Huisgen and H. Rist, *Ann.*, **594**, 137 (1955), have also noted this similarity.

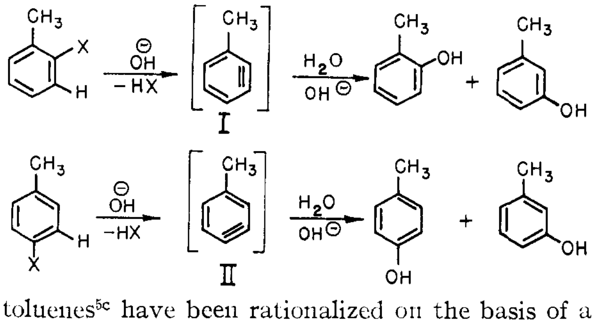
(7) A. Lüttringhaus and D. Ambros, *Ber.*, **89**, 463 (1956), have used the benzyne mechanism to account for the formation of the several side products obtained from the hydrolysis of chlorobenzene.

(8) K. H. Meyer and F. Bergius, *ibid.*, **47**, 3155 (1914).

(9) W. J. Hale and E. C. Britton, *Ind. Eng. Chem.*, **20**, 114 (1928).

(10) Arguments previously given[5b] against other possible intermediates in the amination reaction also apply here.

The alternative amination mechanisms presented by A. A. Morton, *J. Org. Chem.*, **21**, 593 (1956), are too vague to merit serious consideration. It should be noted that the intermediate proposed by Morton to account for the rearrangement with ^{14}C-labeled chlorobenzene is, in effect, *o*-phenylenediamine with a hydride ion coördinated between the 1- and 2-positions. Such an arrangement, with four electrons shared among three mutually overlapping orbitals, is predicted to be highly unfavorable on quantum mechanical grounds.



halotoluenes are dehydrohalogenated to form 3-methylbenzyne (I) and 4-methylbenzyne (II), respectively, which react with hydroxide ion to form mixtures of cresols (as cresolate ions). The orientations observed in amination reactions of halotoluenes[5c] have been rationalized on the basis of a slow addition of amide ion to the benzyne intermediate followed by a fast abstraction of a proton from the solvent or an intramolecular proton shift. The direction of addition to a substituted benzyne is predicted on this basis to lead to the more favorable location of the negative charge in consideration of the inductive effect of the substituent. By analogy, II might be expected to add hydroxide ion preferentially at the *meta*-position while I should prefer to react at the *ortho*-position (assuming steric hindrance to be unimportant). Actually, in halotoluene hydrolyses, the methyl group appears to have considerably less net directing power than in aminations because *o*- and *p*-halotoluenes at 340° with 4 *M* sodium hydroxide give roughly equal amounts of normal and rearranged products. Nonetheless, the cresol compositions resulting from hydrolysis are quite similar to the toluidine compositions from amination and this is all the more striking when the differences in reaction conditions, particularly the temperature (~370°), are considered.

A small amount of direct substitution may be occurring in hydrolyses of *p*-halotoluenes at 340°. However, such processes probably cannot account for more than 2–3% of the cresols formed because *p*-chlorotoluene gave the same product composition at 360° with 4 *M* sodium hydroxide and at 340° with 4 *M* potassium hydroxide. The latter result is especially significant since 4 *M* potassium hydroxide gave almost double the amount of rearrangement as 4 *M* sodium hydroxide at 250°. If not more than 3% of the cresols obtained from the *p*-halotoluenes (and *o*-halotoluenes) at 340° are formed by direct substitution, then from 5–25% of the *m*-cresol formed from the *m*-halotoluenes at 340° must be formed by direct substitution. This follows from the fact that 3-methyl- and 4-methylbenzynes give approximately equimolal mixtures of *o*- and *m*-cresols and *m*- and *p*-cresols, respectively. If all of the reaction were to proceed by elimination–addition with *m*-halotoluenes, the products would be expected in each case to contain about 50% of *m*-cresol. As will be shown later, some direct substitution seems to occur when chlorobenzene is hydrolyzed with 4 *M* sodium hydroxide solution at 340°.

Considerable direct substitution was observed for the hydrolyses of halotoluenes at 250°. The iodotoluenes gave consistently more direct substitution than the corresponding bromotoluenes. *p*-Chlorotoluene gave only a 0.3% yield of cresol when hydrolyzed under identical conditions. The cresol mixtures from two similar runs contained a considerable amount of *m*-cresol (40–50%) as well as a small amount of phenol which made quantitative analysis of the cresols difficult. When *p*-chlorotoluene was hydrolyzed in a manganese steel reaction vessel, the yield was raised to 1.2% and 3.6% for reaction times of two and six hours, respectively. In the first experiment, 4 *M* sodium hydroxide gave 14.4% rearrangement, while in the second, 1 *M* sodium hydroxide gave 9% rearrangement. No similar change in product composition was observed when *m*-chlorotoluene was hydrolyzed similarly at 300°.

Direct substitution was found to be the main reaction path at 340° with 4 *M* sodium acetate solution as the hydrolytic medium. *p*-Bromotoluene gave a 33% yield of spectrophotometrically pure *p*-cresol and *p*-chlorotoluene gave a 6% yield of a mixture of 95% *p*- and 5% *o*-cresols.

The amount of rearrangement at 250° for the three bromotoluenes and the three iodotoluenes decreases with increasing distance of the halogen from the methyl group. Thus the proportion of reaction occurring *via* the benzyne mechanism is 85, ~51 and 47% for *o*-, *m*- and *p*-bromotoluene, respectively; and 63, <33 and <6% for *o*-, *m*- and *p*-iodotoluene, respectively. This behavior indicates that the direct substitution reaction proceeds by an SN2-type mechanism. The inductive effect (+I) of the methyl group would be expected to retard an SN2 reaction, the effect falling off with the distance between the groups. The methyl group might also be expected to retard SN2-type attack at the *ortho*-position through its steric effect.

The possibility of an SN1-type mechanism for the direct reaction would seem ruled out by the fact that *p*-iodotoluene failed to yield any cresols with 4 *M* sodium iodide solution at 340°. In an earlier experiment, no cresols were obtained when *p*-iodotoluene was treated with 4 *M* sodium chloride solution at the same temperature. However, Dr. J. F. Bunnett has suggested that the iodocompound could have been converted to *p*-chlorotoluene which would be expected to be much less readily hydrolyzed. This direct displacement of iodide by chloride does in fact occur since the recovered neutral fraction contained *p*-chlorotoluene. However the failure of cresols to be formed in the presence of sodium iodide argues against the SN1-type reaction path unless one is willing to allow operation of a very large common ion rate depression. It is interesting to note that the reactivity order I > Br > Cl found for the direct displacement reaction shows that breaking of the carbon–halogen bond is well under way in the transition state.[11]

Chlorobenzene-1-^{14}C[12] was found to hydrolyze at 340° with 4 *M* sodium hydroxide solution to yield 58 ± 1% phenol-1-^{14}C and 42 ± 1% phenol-

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[11] G. S. Hammond and L. R. Parks, THIS JOURNAL, **77**, 340 (1955).

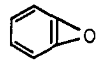
[12] M. Fields, M. A. Leaffer and J. Rohan, *Science*, **109**, 35 (1949); obtained from Tracerlab, Inc., on allocation by the U. S. Atomic Energy Commission.

2-^{14}C. If only the benzyne mechanism were operative, equal quantities of the two phenols should have been formed in the absence of a ^{12}C-^{14}C kinetic isotope effect which might tend to favor formation of phenol-2-^{14}C. The discrepancy is undoubtedly due to occurrence of the SN2-type reaction which was shown earlier to be of importance in the hydrolysis of *m*-halotoluenes. The contribution to the extent of rearrangement resulting from the hydrolysis of diphenyl ether[9] is not known. Diphenyl ether might be formed by a direct displacement between phenolate ion and chlorobenzene or from a combination of phenolate ion and benzyne.[7] The diphenyl ether could hydrolyze by either rearranging or non-rearranging reactions. The fact that the ditolyl ethers are more difficultly hydrolyzed than diphenyl ether under the reaction conditions[4] makes it unlikely that the 5–25% direct displacement postulated for the *m*-halotoluenes at 340° is due to a non-rearranging formation and hydrolysis of ditolyl ethers. The mechanisms of diaryl ether formation and cleavage during the hydrolyses of aryl halides awaits further study.

The variation of the product composition with reaction temperature indicates the direct and elimination–addition reactions have quite different temperature coefficients. It is not known to what extent the profound temperature effects can be associated with the fact that the reactions are very likely to be heterogeneous. Shreve and Marsel[4] observed no change in reaction velocity in the presence of emulsifying agents and felt that the reaction might be homogeneous. However, it was allowed that the emulsifying agents may have been ineffective in the presence of hot concentrated alkali.

The variation of product composition with temperature satisfactorily accounts for the small differences between our results and those reported by Shreve and Marsel[4] for experiments in which the reaction mixtures were shaken during the heating and cooling periods. The character of the effect associated with this seemingly minor difference in procedure may be illustrated as follows. Chlorobenzene-1-^{14}C was hydrolyzed with 6 *M* sodium hydroxide solution in a stainless steel bomb at 330° for 2.5 hours, the reaction mixture being shaken during the heating and cooling periods as well as at the reaction temperature. Only 7% rearrangement was observed. However, *p*-chlorotoluene, when hydrolyzed in a stainless steel bomb with shaking only at 320 ± 15° with 6 *M* sodium hydroxide solution for two hours, gave the customary 50% of rearrangement product.

The dual mechanism here postulated for the hydrolysis of the halotoluenes and chlorobenzene satisfactorily explains the behavior of the chlorobiphenyls on hydrolysis with different bases. When sodium carbonate solution was used, no rearrangement was observed,[13] while sodium hydroxide solution gave rearranged products.[14] Exceptional behavior is observed during the hydrolysis of *o*-chlorophenolate ion[15] with sodium hydroxide solution and/or strontium hydroxide solution in that only pyrocatechol is formed. The negatively charged oxygen atom *ortho* to the leaving chlorine could very well retard both the benzyne and the SN2-type reactions. A possible alternative would be frontside displacement of the chloride by the oxygen to give "benzyne oxide" (III). Such an intermediate could account for the exclusive formation of pyrocatechol as the hydrolysis product.



III

Experimental

The halotoluenes were redistilled Eastman or Matheson, Coleman and Bell products. As far as could be judged from their infrared spectra each contained none of its isomers. The chlorobenzene-1-^{14}C was the same material used previously.[5a] The cresols employed as standards for infrared analyses were center cuts of redistilled Eastman products. The infrared spectrum of each cresol was identical with those published elsewhere.[16]

The radioactive analyses were made using the vibrating-reed electrometer method of Neville.[17] The infrared spectra were taken with a Perkin–Elmer (Model 21) double-beam spectrophotometer.

Analysis of Cresol Mixtures.—The cresol mixtures were analyzed by means of their infrared spectra in carbon disulfide solution.[18] Measurements were made at 9.04, 10.77 and 11.84 μ for mixtures of *o*- and *m*-cresols and at 10.77, 12.23 and 12.88 μ for mixtures of *m*- and *p*-cresols. The optical density was found to be linear with mole fraction at each of the above wave lengths. Mixtures of the three cresols were analyzed with the aid of measurements at 10.77, 12.23 and 12.88 μ.

Halotoluene Hydrolyses. A. Sodium Hydroxide Solutions.—The following procedure is typical. A mixture of 20.1 g. of *p*-chlorotoluene and 250 ml. of 4 *M* sodium hydroxide solution contained in a monel liner was sealed in a manganese steel hydrogenation bomb. The bomb was heated to 340° in 2 hours in a conventional electrically heated jacket with the temperature controlled by a Leeds–Northrup Micromax regulator and a calibrated iron–constantan thermocouple. The reaction mixture was then shaken at 340 ± 4° for 2 hours and allowed to cool overnight.[19] The contents of the liner (245 ml.) were extracted three times with 50-ml. portions of ether, cooled in an ice-bath and cautiously acidified with concentrated hydrochloric acid. The resulting mixture was extracted three times with 50-ml. portions of ether. The combined extracts were dried, the ether was removed and the residual cresol mixture was distilled through a semimicro column.[20] The distillate, b.p. 72–74° (5 mm.), amounted to 10.1 g. (59%) and was shown by its infrared spectrum to contain 50.5% *m*-cresol and 49.5% *p*-cresol.

The distillation residues were usually less than 0.25 g. except with iodotoluenes which gave residues of 0.5–0.7 g. These fractions and the non-phenolic reaction products were not investigated. Where effort was made to recover the unreacted starting material, material balances of about 90% were obtained. Several mixtures of cresols were prepared and carried through the isolation procedure, one being subjected to the reaction conditions. Between 85 and 90% of each cresol mixture was recovered. The composi-

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[13] E. C. Britton, U. S. Patent 1,959,283; *Chem. Zentr.*, **105**, **II**, 1088 (1934).

[14] J. E. Moose, U. S. Patent 1,979,116; *C. A.*, **29**, 182 (1935).

[15] A. I. Kipriyanov and E. D. Suich, *Ukrain. Khem. Zhur.*, **7**, 94 (1932); *C. A.*, **27**, 3824 (1933); S. G. Burroughs, U. S. Pat. 2,041,592; *C. A.*, **30**, 4513 (1936).

[16] R. A. Friedel, THIS JOURNAL, **73**, 2881 (1951); "American Petroleum Institute Research Project 44," Carnegie Institute of Technology, Pittsburgh, Pa., 1952, No. 1433–1435.

[17] O. K. Neville, THIS JOURNAL, **70**, 3499 (1948).

[18] J. J. Heigl, M. F. Bell and J. U. White, *Anal. Chem.*, **19**, 293 (1947).

[19] Considerable residual pressure was noted only for the iodotoluenes and bromotoluenes when hydrolyzed at 340°.

[20] C. W. Gould, Jr., G. Holzman and C. Niemann, *Anal. Chem.*, **20**, 361 (1948).

tions of these mixtures agreed to within 2% of the compositions of the original mixtures.

B. **Sodium Acetate Solution.**—A description of a typical experiment follows. A mixture of 20.1 g. of *p*-chlorotoluene and 250 ml. of 4 *M* sodium acetate solution was shaken for 2 hours at 340°. The reaction mixture remaining in the liner (233 ml.) was extracted three times with 50-ml. portions of ether. The combined extracts were extracted three times with 30-ml. portions of 1 *N* sodium bicarbonate solution, washed with 30 ml. of water and extracted three times with 30-ml. portions of 1 *M* sodium hydroxide solution. The sodium hydroxide solution was acidified with 6 *M* hydrochloric acid and extracted three times with 30-ml. portions of ether. The combined extracts were dried, the ether was removed and the residual cresol mixture was distilled through a semimicro column.[20] The distillate, b.p. 56–62° (2 mm.), weighed 0.98 g. (6.1%) and was found to consist of 5% *m*-cresol and 95% *p*-cresol. A mixture of 15.7% *m*-cresol and 84.3% *p*-cresol was carried through the reaction conditions and isolated as above. The infrared spectrum of the product indicated it to contain 11.8% *m*-cresol.

Attempted Hydrolysis of *p*-Iodotoluene with 4 *M* Sodium Iodide and 4 *M* Sodium Chloride Solutions.—A mixture of 20.0 g. of *p*-iodotoluene and 250 ml. of 4 *M* sodium iodide solution was shaken at 340° for 10 hours. A tarry acidic fraction of 45 mg. was obtained. The infrared spectrum of this fraction in carbon disulfide solution failed to indicate the presence of cresols. Similar treatment of 20.1 g. of iodotoluene with 4 *M* sodium chloride solution for 2 hours also yielded no cresols. The infrared spectrum of the crude recovered neutral material showed all the bands with the same relative intensities possessed by *p*-chlorotoluene but no band at 12.57 μ as is characteristic of *p*-iodotoluene. Considerable decomposition occurred during both attempted hydrolyses.

Hydrolysis of Chlorobenzene-1-^{14}C.—The labeled chlorobenzene[12] (19.7 g.) was hydrolyzed with 250 ml. of 4 *M* sodium hydroxide solution at 340°. The reaction mixture remaining in the liner (233 ml.) was treated in the usual manner. The neutral fraction consisted of 0.15 g. of starting material, 0.30 g. of diphenyl ether, b.p. 74–95° (0.7 mm.), and about 10 mg. of a dark residue. The crude acidic fraction amounted to 13.0 g. (79%), 0.2 g. of which was probably a mixture of hydroxybiphenyls.[9] The crude phenol-*X*-^{14}C was hydrogenated in absolute alcohol over platinic oxide and yielded 8.9 g. (66%) of cyclohexanol-*X*-^{14}C; b.p. 159.0–159.4° (741 mm.), n^{25}D 1.4629. The cyclohexanol was degraded[5b] to 1,5-diaminopentane which was isolated as the dibenzenesulfonamide, m.p. 118.2–118.7 (lit.[21] m.p. 119°) after 5 recrystallizations from ethanol, and carbon dioxide (collected as barium carbonate). The specific activity of the phenol-X-^{14}C was taken as equal to the activity of the 2,4-dinitrophenylhydrazone of cyclohexanone-X-^{14}C, m.p. 160.6–161.1° (lit.[22] m.p. 162°) after 4 recrystallizations from ethanol. The ^{14}C results are summarized in Table II.

1,5-Diaminopentane (0.28 g.) was oxidized[5b] in 19% yield to glutaric acid with potassium permanganate; unlabeled glutaric acid was added to the reaction mixture as a carrier. The glutaric acid-X-^{14}C was assayed as the di-*p*-bromophenacyl ester, m.p. 136.7–137.4° (lit.[23] m.p. 136.8°) after 3 recrystallizations from ethanol. The glutaric acid was degraded[5b] to 1,3-diaminopropane, isolated as the dibenzamide, m.p. 147.6–149.0° (lit.[5b] m.p. 150.0–150.5°) after one recrystallization from cyclohexane.

TABLE II

RADIOACTIVITY DETERMINATIONS OF DEGRADATION PRODUCTS OF PHENOL-X-^{14}C FROM HYDROLYSIS OF CHLOROBENZENE-1-^{14}C

Compound	Activity[a]	%Total act.
Phenol-X-^{14}C	0.2908 ± 1.1%	(100)
1,5-Diaminopentane	.1207 ± 1.5%	41.5 ± 0.8
Carbon dioxide	.1644 ± 0.9%	56.5 ± 0.8[b]
Glutaric acid	.0227 ± 1.3%[c]	(41.5)[d]
1,3-Diaminopropane	.00028 ± 100%	0.6 ± 0.6

[a] μc./mmole. [b] Possibly low by 0.4–2.0%.[5b] [c] The 1,5-diaminopentane was substantially diluted during the oxidation. [d] Assumed to be the same as the 1,5-diaminopentane.

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(21) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 3rd Ed., 1948, p. 234.

(22) Reference 21, p. 262.

(23) E. H. Huntress and S. P. Mulliken, "Identification of Pure Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1941, p. 98.

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[CONTRIBUTION NO. 2150 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

The Products from the Reaction of N-(2-Bromoallyl)-ethylamine with Sodium Amide[1]

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The principal product obtained from N-(2-bromoallyl)-ethylamine and sodium amide in liquid ammonia has been shown to be N-ethylallenimine (I) as proposed by Ettlinger and Kennedy rather than N-ethylallylideneamine (II). N-Ethylpropargylamine (III) was also isolated in small yield from this reaction. III was obtained in 71% yield by treatment of N-(2-chloroallyl)-ethylamine with potassium amide in liquid ammonia.

Pollard and Parcell,[3] in an attempt to extend their synthesis of N,N-dialkylpropargylamines[4] to N-alkylpropargylamines, treated N-(2-bromoallyl)-ethylamine with sodium amide in liquid ammonia. The main product was shown by its infrared spectrum not to be the expected N-ethylpropargylamine (III), and the isomeric N-ethylallylideneamine structure (II) was assigned.[5] This compound rapidly took up two moles of hydrogen to yield N-ethyl-*n*-propylamine. With hydrochloric acid, the compound was hydrolyzed to ethylamine and a chlorine-containing "aldehyde" which reduced Fehling solution, formed a silver mirror with Tollens reagent but could not be isolated in pure form. When hydrolyzed with dilute hydrochloric acid in the presence of 2,4-dinitrophenylhydrazine, the compound yielded a derivative which melted at 124–125° and was reported to contain 50.89% C, 3.85% H and 12.03% Cl.

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(1) Supported in part by a grant from the National Science Foundation.

(2) National Science Foundation Predoctoral Fellow, 1954–1957.

(3) C. B. Pollard and R. F. Parcell, THIS JOURNAL, **73**, 2925 (1951).

(4) R. F. Parcell and C. B. Pollard, *ibid.*, **72**, 2385, 3312 (1950).

(5) The absence of N-ethylaminoallene was indicated by the lack of nitrogen–hydrogen stretching absorption at about 3230 cm.$^{-1}$. V. A. Engelhardt, *ibid.*, **78**, 107 (1956), has recently observed rapid base-catalyzed isomerizations of allenic amines to acetylenic amines and concluded that these reactions probably proceed by way of carbanion intermediates as postulated by T. L. Jacobs, R. I. Akawie and R. G. Cooper, *ibid.*, **73**, 1273 (1951).