For the hydrolysis in acid medium, the sample was diluted with water, the calculated amount of 0.25 *N* hydrochloric acid added and then further diluted to the mark with water. Aliquots were titrated with either 0.1 or 0.025 *N* sodium hydroxide to methyl red end-point.

General Esterification Procedure.—Equal molar amounts of the appropriate amine and boric acid were weighed directly into a volumetric flask and diluted to the mark with freshly boiled distilled water previously maintained at 25°. Aliquots periodically removed from the 25° solutions were titrated with 0.025 *N* hydrochloric acid to the methyl red end-point.

Acknowledgment.—The authors would like to acknowledge the value of stimulating discussions with Prof. S. Winstein, Dr. A. L. McCloskey and Dr. W. G. Woods.

ANAHEIM, CALIF.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS, THE STATE UNIVERSITY]

An Oxygen-18 Tracer Study of the Isomerization of Cyclopropylcarbinyl Benzenesulfonate

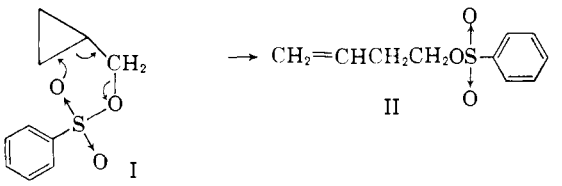
BY DONALD B. DENNEY AND EUGENE J. KUPCHIK[1]

RECEIVED JULY 31, 1959

Cyclopropylcarbinyl benzenesulfonate (I), labeled with excess oxygen-18 in the ether position of the ester group, was isomerized at *ca.* 90° to 3-butenyl benzenesulfonate (II). Hydrogenation of II followed by reductive cleavage with sodium in liquid ammonia gave *n*-butyl alcohol which contained one-third of the excess oxygen-18 originally present in I. Compound I was also found to isomerize to cyclobutyl benzenesulfonate (III) at room temperature. Reductive cleavage of III with sodium in liquid ammonia gave cyclobutanol which contained one-third of the excess oxygen-18 originally present in I. These results show that complete equilibration of the excess oxygen-18 occurred during the isomerization of I to II and I to III. The mechanistic implications of these results are discussed.

The chemistry of small ring compounds has been the subject of considerable research during the past decade. One of the most interesting aspects of this subject has been the facile interconversion of cyclopropylcarbinyl, cyclobutyl and allycarbinyl derivatives. The more recent developments and their theoretical implications have been discussed in considerable detail.[2]

Bergstrom and Siegel[3] have observed that cyclopropylcarbinyl benzenesulfonate (I), in contact with anhydrous potassium carbonate at 20°, isomerizes to the extent of 90% in 24 hours to a mixture which consists predominately of 3-butenyl benzenesulfonate (II). These workers suggested that II may have been formed by an intramolecular rearrangement.



Infrared and other analytical data indicated that a second substance, isomeric with II, was present in the crude isomerization product. This second substance was presumed to be cyclobutyl benzenesulfonate.

It was the purpose of this research to examine more closely the products of this isomerization in the hope of confirming the formation of cyclobutyl benzenesulfonate. It was also hoped that information concerning the mechanism of this reaction could be obtained by studying the isomerization of cyclopropylcarbinyl benzenesulfonate, labeled with excess oxygen-18 in the ether position of the ester group.

In an initial attempt to isomerize I to II, a methylene chloride solution of labeled I was allowed to remain in contact with anhydrous potassium carbonate at room temperature for 65 hours. The infrared spectrum of the product differed markedly from that of an authentic sample of 3-butenyl benzenesulfonate. For example, whereas the latter compound had an absorption band at 6.1 μ, due most probably to the isolated carbon–carbon double bond, the product did not have a band in this region. Furthermore, on attempted hydrogenation of the product in methanol with 10% palladium-on-charcoal as the catalyst, only 11.1% of the theoretical quantity of hydrogen was absorbed. A known sample of 3-butenyl benzenesulfonate easily absorbed the theoretical quantity of hydrogen. The absorption band at 6.1 μ was completely absent after hydrogenation. The infrared spectrum of the hydrogenated material was essentially identical to that of an authentic sample of *n*-butyl benzenesulfonate.

In another attempt to isomerize I to II, a sample of I (no solvent) was allowed to remain in contact with anhydrous potassium carbonate for 68 hours at room temperature. No absorption band at 6.1 μ appeared in the infrared; however, changes in the spectrum did occur. This was shown to be due to the formation of cyclobutyl benzensulfonate.

The isomerization of labeled I to II was finally accomplished by heating a mixture of labeled I (no solvent) and anhydrous potassium carbonate on a steam-bath for 7 hours. The isomerization was followed by observing the appearance of the absorption band at 6.1 μ. The infrared spectrum of the product was essentially identical to that of an authentic sample of 3-butenyl benzenesulfonate. The yield was 77.7%. Since gas appeared to be evolved during the reaction, it appears likely that some elimination occurred with the formation of

(1) Alfred P. Sloan Fellow in Chemistry, 1956–1957; E. I. du Pont Teaching Fellow, 1957–1958.

(2) J. D. Roberts, Abstracts, Sixteenth National Organic Chemistry Symposium, Seattle, Wash., pp. 1–10.

(3) C. G. Bergstrom and S. Siegel, THIS JOURNAL, **74**, 145 (1952).

butadiene. It is interesting to note that the conditions required for this isomerization were considerably more strenuous than those used by Bergstrom and Siegel.[3] Since these reactions are particularly sensitive to catalysis by acids,[4] it may well be that Bergstrom and Siegel had trace amounts of acid present which led to the greater rate of reaction observed by them.

On hydrogenation of the labeled 3-butenyl benzenesulfonate in ethanol with 10% palladium-on-charcoal as the catalyst, the theoretical quantity of hydrogen was consumed, but only a 58.5% yield of labeled *n*-butyl benzenesulfonate was obtained. The reason for this low yield is not known.

As mentioned above it was found that labeled I (no solvent) in contact with anhydrous potassium carbonate at room temperature isomerized to cyclobutyl benzenesulfonate. The infrared spectrum of the product indicated that little or no 3-butenyl benzenesulfonate or cyclopropylcarbinyl benzenesulfonate was present. The absence of 3-butenyl benzenesulfonate was indicated by the fact that no strong band at 6.1 μ, due to the isolated carbon–carbon double bond, was present. The apparent absence of cyclopropylcarbinyl benzenesulfonate was indicated by the fact that several strong bands in the spectrum of cyclopropylcarbinyl benzenesulfonate were completely absent in the isomerized product.

In order to determine the amount of oxygen-18 in the ether position of the ester group of the labeled *n*-butyl benzenesulfonate and of the labeled cyclobutyl benzenesulfonate, it was necessary to convert these compounds to the corresponding alcohols by a process which would not equilibrate the oxygen-18. It has been shown that sodium in liquid ammonia reduces *p*-toluenesulfonates quite smoothly to the parent alcohols.[5] It has been further shown that under these conditions 2-phenyl-1-propyl *p*-bromobenzenesulfonate, labeled with excess oxygen-18 in the ether position of the ester group, is converted to the corresponding alcohol with no loss of oxygen-18.[6]

Reductive cleavage of the labeled *n*-butyl benzenesulfonate by the above procedure gave a 22.4% yield of labeled *n*-butyl alcohol (VI). Reductive cleavage of the labeled cyclobutyl benzenesulfonate gave a 22.0% yield of labeled cyclobutanol (VII).

Determination of the oxygen-18 content in the above labeled compounds (Table I) revealed that the oxygen-18 in both the 3-butenyl benzenesulfonate and cyclobutyl benzenesulfonate was essentially completely randomized.

The results of this research definitely rule out the mechanism postulated by Bergstrom and Siegel. If the isomerization of I to II proceeded by the intramolecular mechanism depicted above, then none of the excess oxygen-18 would have been found in the ether position of the ester group in II. The oxygen-18 equilibration and the formation of either 3-butenyl benzenesulfonate or cyclobutyl benzenesulfonate from cyclopropylcarbinyl benzenesulfonate can be explained in several ways.

(4) Prof. J. D. Roberts, private communication.

(5) D. B. Denney and B. Goldstein, *J. Org. Chem.*, **21**, 419 (1956).

(6) D. B. Denney and B. Goldstein, THIS JOURNAL, **79**, 4948 (1957).

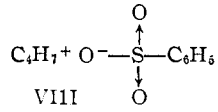
TABLE I

OXYGEN-18 ANALYTICAL DATA[a]

Compound	Atom % excess oxygen-18 in labeled position
Cyclopropanecarboxylic acid (IV)	1.15, 1.18[b]
Anilide of IV	1.20, 1.21
Phenylurethan of cyclopropylmethanol (V)	1.18, 1.20
Phenylurethan of VI	0.43, 0.44[c]
Phenylurethan of VII	0.44, 0.44[c]

[a] The analyses were carried out according to the method of W. E. Doering and E. Dorfman, THIS JOURNAL, **75**, 5595 (1953), as modified by D. B. Denney and M. A. Greenbaum, *ibid.*, **79**, 979 (1957). [b] Each oxygen of the carboxyl group contains this amount of excess oxygen-18. [c] The values found indicate that 96% equilibration has occurred. However, since the experimental error in the oxygen-18 determination is usually ±0.01 atom % oxygen-18, it has been assumed that the data represent essentially complete equilibration.

Perhaps the simplest explanation is that I ionizes to an external ion-pair (VIII) which is in rapid equilibrium with I and III and is slowly converted



VIII

to II. On the other hand, rapid equilibrium between I and III *via* an internal ion pair could also lead to complete equilibration; further isomerization to II would then proceed through VIII but at a lower rate than for the I ⇄ III interconversion. Several other modified descriptions of these processes can be written. The data as it now stands do not appear to distinguish between any of them. Perhaps the most interesting observation is the finding that the cyclobutyl benzenesulfonate is completely equilibrated. It seemed quite possible that this would not be the case. Clearly more work is needed before it can be decided whether 100% equilibration occurs with every conversion of I to III or whether it is a product of a rapid and partially equilibrating equilibrium between I and III.

It is interesting to note that the rate sequence and thermodynamic stabilities of the three compounds studied here are in agreement with those found for other derivatives of these materials.[2]

Nothing has been said about the cation or cations involved in these rearrangements, since this work does not add any new information to that aspect of the subject. Roberts[2] has considered in detail the possible structures for these ions.

Experimental[7]

Cyclopropanecarboxylic Acid-$CO^{18}O^{18}H$ (IV).—Water (86.4 g., 4.8 moles) containing *ca.* 1.7 atom % oxygen-18 was added over 0.75 hour with stirring to 167.0 g. (1.60 moles) of cyclopropanecarbonyl chloride.[8] The mixture was heated on a steam-bath with stirring for 38.5 hours and then was extracted with two 500-ml. portions of anhydrous ether. The ether extracts were dried over Drierite. The ether was removed by distillation, and the residue was vacuum distilled. There was obtained 116.7 g. (86.0%) of cyclopropanecarboxylic acid-$CO^{18}O^{18}H$ (IV), b.p. 94–95° (26 mm.) [lit.[9] 94–95° (26 mm.)].

(7) Microanalyses were by G. Robertson, Florham Park, N. J. Unless otherwise stated, all melting points were determined by use of the Kofler hot-stage microscope and are uncorrected.

(8) G. H. Jeffery and A. I. Vogel, *J. Chem. Soc.*, 1804 (1948).

(9) C. M. McCloskey and G. M. Coleman, "Organic Syntheses," Coll. Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1955, p. 221.

The anilide derivative of IV was prepared: Compound IV (0.86 g., 0.01 mole) was allowed to react with 1.43 g. (0.012 mole) of thionyl chloride. The mixture was heated on a steam-bath for 0.5 hour. A solution of 3.22 g. (0.02 mole) of aniline in 30 ml. of benzene was added, and the mixture was heated on a steam-bath for 0.5 hour. The mixture was extracted with 5% hydrochloric acid solution, 5% sodium hydroxide solution and water. The benzene was evaporated, and the residue was recrystallized twice from 95% ethanol. The anilide had m.p. 112–112.5° (lit.[10] 110–111°).

Labeled Cyclopropylmethanol (V).—A solution of 113.1 g. (1.32 moles) of cyclopropanecarboxylic acid-$CO^{18}O^{18}H$ (IV) in 500 ml. of anhydrous ether was added over 3 hours with stirring to a mixture of 66.2 g. (1.74 moles) of lithium aluminum hydride and 500 ml. of anhydrous ether. The mixture was then stirred for 17 hours. Water (250 ml.) was added while the mixture was cooled with an ice–water-bath. Ether (500 ml.) and 750 ml. of water were added. The mixture was then shaken with 2 liters of 10% sulfuric acid solution. The ether layer was removed, and the aqueous layer was extracted with two 1-liter portions of ether and one 500-ml. portion of ether. The combined ether extracts were dried over anhydrous magnesium sulfate. The ether was removed by distillation. Distillation of the residue yielded 44.2 g. (46.3%) of labeled cyclopropylmethanol (V), b.p. 121–123° (lit.[3] 124°).

The phenylurethan derivative of V was prepared by allowing 1.32 g. (0.011 mole) of phenyl isocyanate to react with 0.72 g. (0.010 mole) of V in 7 ml. of hexane. The mixture was warmed on a steam-bath and then cooled. Crystals were obtained. After it was recrystallized three times from hexane, the phenylurethan had m.p. 76.5–77.5° (lit.[11] 75.5–76°).

Labeled Cyclopropylcarbinyl Benzenesulfonate (I).—The procedure was essentially the same as that described by Bergstrom and Siegel[3] for the preparation of unlabeled cyclopropylcarbinyl benzenesulfonate.

Freshly distilled benzenesulfonyl chloride (27.4 g., 0.155 mole) was added over 1.25 hours with stirring to a mixture of 11.2 g. (0.155 mole) of labeled cyclopropylmethanol (V) and 38 ml. of 2,4,6-collidine at 0–5°. Anhydrous methylene chloride (20 ml.) was then added, and the mixture was stirred at 0–5° for 1.5 hours. Then 38 ml. of 10 *N* sulfuric acid was added at a rate which did not allow the temperature to rise above 18°. The methylene chloride layer was removed, and the aqueous layer was extracted with two 75-ml. portions of methylene chloride. The combined methylene chloride extracts were washed with three 75-ml. portions of 2.5 *N* sulfuric acid, two 100-ml. portions of water and then were dried over anhydrous potassium carbonate for 45 hours. The methylene chloride was removed *in vacuo* in a nitrogen atmosphere. There was obtained 30.3 g. of crude labeled cyclopropylcarbinyl benzenesulfonate (I). An attempt to purify a sample of this material by vacuum distillation resulted in its decomposition. It was decided, therefore, to study the isomerization of crude labeled I.

The infrared spectrum differed in many respects from that of 3-butenyl benzenesulfonate. There was no absorption band at 6.1 μ. This band was present in the spectrum of 3-butenyl benzenesulfonate and is probably due to the isolated carbon–carbon double bond.

An attempt was made to hydrogenate a sample of labeled I. A methylene chloride solution of this particular sample had remained in contact with anhydrous potassium carbonate for 65 hours. A microhydrogenation apparatus was used. A stirred solution of 1.00 g. (0.00472 mole) of this sample in 25 ml. of methanol in contact with 0.10 g. of 10% palladium-on-charcoal absorbed 12.8 ml. of hydrogen at 25° and 768.7 mm. (theroretical amount for 0.00472 mole of 3-butenyl benzenesulfonate plus catalyst is 115.5 ml.).

3-Butenyl Benzenesulfonate.—The procedure was the same as that described above for the preparation of labeled cyclopropylcarbinyl benzenesulfonate (I). From 11.2 g. (0.155 mole) of 3-butene-1-ol[3] and 27.4 g. (0.155 mole) of benzenesulfonyl chloride there was obtained 33.0 g. of crude 3-butenyl benzenesulfonate which was not further purified. The infrared spectrum had an absorption band at 5.8 μ, which indicates some degree of contamination by a carbonyl-containing compound. This band was also present in the 3-butene-1-ol employed. A band at 6.1 μ was present. This band can be ascribed to the carbon–carbon double bond.

Isomerization of Labeled Cyclopropylcarbinyl Benzenesulfonate (I) to 3-Butenyl Benzenesulfonate.—A mixture of 30.1 g. (0.142 mole) of labeled cyclopropylcarbinyl benzenesulfonate (I) and 7.5 g. of anhydrous potassium carbonate was heated on a steam-bath for 7 hours. Some gas was evolved. The mixture was filtered, and the residue was washed with methylene chloride. The methylene chloride was removed from the filtrate *in vacuo* in a nitrogen atmosphere. There was obtained 23.4 g. (77.7%) of labeled 3-butenyl benzenesulfonate. The infrared spectrum was exactly identical to that of the 3-butenyl benzenesulfonate prepared independently except that it did not have an absorption band at 5.8 μ.

Hydrogenation of Labeled 3-Butenyl Benzenesulfonate.—The hydrogenation was performed using a Parr low pressure reaction apparatus. The labeled 3-butenyl benzenesulfonate (23.4 g., 0.11 mole) was dissolved in 100 ml. of ethanol, and 2.34 g. of 10% palladium-on-charcoal was used as the catalyst. The theoretical amount of hydrogen was consumed in 10 minutes. The mixture was filtered, and the residue was washed with methylene chloride. The solvent was removed from the filtrate *in vacuo* in a nitrogen atmosphere. A solution of the residue in 150 ml. of methylene chloride was washed with 50 ml. of 5% sodium bicarbonate solution and 100 ml. of water and then was dried over anhydrous potassium carbonate. The methylene chloride was removed *in vacuo* in a nitrogen atmosphere. There was obtained 13.8 g. (58.5%) of labeled *n*-butyl benzenesulfonate. The infrared spectrum was essentially identical to that of an authentic sample of *n*-butyl benzenesulfonate.

Reductive Cleavage of Labeled *n*-Butyl Benzenesulfonate.—To a stirred solution of 8.90 g. (0.387 mole) of sodium in 250 ml. of liquid ammonia, there was added over 0.5 hour a solution of 13.80 g. (0.0645 mole) of labeled *n*-butyl benzenesulfonate in 100 ml. of anhydrous ether. The mixture was stirred for 6 hours and then solid ammonium chloride was added in small portions until the blue color was discharged. Water (25 ml.) was added, and the ammonia was allowed to evaporate. Water (100 ml.) was then added, and the ether layer was removed. The aqueous layer was extracted with six 50-ml. portions of ether. The combined ether extracts were dried over anhydrous sodium sulfate. The ether was removed by distillation through a 50 cm. coiled-wire fractionating column. Distillation of the residue from a 10-ml. distilling flask afforded 1.07 g. (22.4%) of labeled *n*-butyl alcohol (VI), b.p. 112–118° (lit.[12] 117.4°). The infrared spectrum was identical to that of an authentic sample of *n*-butyl alcohol.

The phenylurethan derivative of VI was prepared as described above for labeled cyclopropylmethanol (V), by allowing 1.32 g. (0.011 mole) of phenyl isocyanate to react with 0.74 g. (0.010 mole) of V. After it was recrystallized four times from hexane, the phenylurethan had m.p. 62–63° (lit.[12] 61°). Admixture with an authentic sample did not depress the melting point.

Isomerization of Labeled Cyclopropylcarbinyl Benzenesulfonate (I) to Labeled Cyclobutyl Benzenesulfonate.—Labeled cyclopropylcarbinyl benzenesulfonate (I) (28.5 g., 0.134 mole) was allowed to remain in contact with 7.0 g. of anhydrous potassium carbonate for 63 hours at *ca.* 25°. At the end of this time new bands were present in the infrared at 11.1 and 8.0 μ. A band at 12.4 μ had disappeared, and a band initially at 9.7 μ appeared to be shifted to 9.55 μ. A band initially at 11.8 μ was now at 11.7 μ. No band at 6.1 μ characteristic of an isolated carbon–carbon double bond was present. The mixture was filtered, and the residue was washed with methylene chloride. The methylene chloride was removed from the filtrate *in vacuo* in a nitrogen atmosphere. There was obtained 24.6 g. of material which was presumed to be crude labeled cyclobutyl benzenesulfonate.

Reductive Cleavage of Labeled Cyclobutyl Benzenesulfonate.—The procedure was identical to that described above for labeled *n*-butyl benzenesulfonate. From 24.6 g. (0.116 mole) of labeled cyclobutyl benzenesulfonate and 16.0 g. (0.696 mole) of sodium there was obtained 1.84 g. (22.0%) of cyclobutanol (VII), b.p. 118–122° [lit.[13] 123°

(10) W. Autenrieth, *Ber.*, **38**, 2534 (1905).

(11) L. I. Smith and S. McKenzie, Jr., *J. Org. Chem.*, **15**, 74 (1950).

(12) I. Heilbron, "Dictionary of Organic Compounds," Vol. I, Oxford University Press, New York, N. Y., 1953, p. 388.

(13) Reference 12, p. 632.

(733 mm.)]. The infrared spectrum differed markedly from that of 3-butene-1-ol. For example, whereas the latter compound had a strong hand at 6.1 μ, due probably to the isolated carbon–carbon double bond, the present material had only a very small band in this region. The present material also lacked bands at 8.45, 9.5, 10.1 and 11.4 μ. Additional bands at 7.5, 8.1, 8.9, 9.1, 9.7 and 10.4 μ were present. The infrared spectrum also differed markedly from that of cyclopropylmethanol. For example, the present material did not have bands at 12.9, 12.4, 11.95 and 11.0 μ. The infrared spectrum compared favorably with that reported in the literature for cyclobutanol.[14]

The phenylurethan derivative of VII was prepared as described above for labeled cyclopropylmethanol (V) by allowing 1.32 g. (0.011 mole) of phenyl isocyanate to react with 0.74 g. (0.010 mole) of VII. After it was recrystallized five times from hexane, the phenylurethan had m.p. 131.5–132.5° (capillary) (lit.[14] 130.6–131.2°).

Anal. Calcd. for $C_{11}H_{13}O_2N$: C, 69.09; H, 6.85; N, 7.33. Found: C, 69.38; H, 7.08; N, 7.19.

(14) J. D. Roberts and C. W. Sauer, THIS JOURNAL, **71**, 3925 (1949).

NEW BRUNSWICK, N. J.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE RICE INSTITUTE]

The Reactions of Diazonium Salts with Nucleophiles. V. The Substitution of Halogen by Thiocyanate[1]

BY EDWARD S. LEWIS AND HARALD SUHR

RECEIVED JUNE 4, 1959

Rates are reported for the reactions of various *o*- and *p*-halogen substituted benzenediazonium ions with thiocyanate, resulting in the substitution of thiocyanate for the halogen. Solvent effects are studied. Although the order of reactivities of *p*-halogen derivatives is *p*-I > *p*-Br > *p*-Cl > *p*-F, it is concluded that the reaction is a normal nucleophilic substitution powerfully activated by the diazonium ion group.

Introduction

Substitution of groups *ortho* and *para* to the diazonium group has long been known; among the earliest examples was that of Hantzsch and Hirsch[2] who found that when *p*-chlorobenzenediazonium thiocyanate was dissolved in alcohol and precipitated with ether, the solid product was *p*-thiocyanatobenzenediazonium chloride. Subsequent investigations by Hirsch[3] established the generality of the reaction, and Hantzsch and his co-workers[4] found that chloride ion would substitute for nuclear bromine *ortho* or *para* to the diazonium group.[4] They found in one case first-order kinetics, which now appears improbable, and also found that the rate was strongly solvent dependent. A large variety of analogous reactions is summarized by Saunders[5] showing that many groups can be lost in such reactions, in most cases from the position *ortho* to the diazonium group.

In their influential review,[6] Bunnett and Zahler made it clear that the diazonium group was a particularly powerful member of a class of substituents which activate nucleophilic aromatic substitutions, which also includes the more familiar nitro group. They observed that the diazonium ion group was the most powerful activator known, in conformity with its very high σ-value.[7] Recently the rates of displacement of halogen *para* to the diazonium group by methoxide ion have been measured.[8] An exploratory experiment showed that the reactions of *p*-chloro- and *p*-fluorobenzenediazonium ion with thiocyanate ion were too slow to measure in water solution.[9] The contrast between this result and those of Hantzsch and his co-workers, and the first-order kinetics reported by Hantzsch for the chloride–bromide exchange prompted a more careful study of this system. The reactivity of thiocyanate in nucleophilic aromatic substitution was not questioned since it had been shown to displace either chloride[10] or the nitro group[11] to give 2,4-dinitrophenylthiocyanate; its reactivity in aliphatic substitutions is also well established.

Methods and Results

The reaction was followed by observing the introduction of radioactivity into the diazonium salt by reaction of a large excess of halodiazonium salt with carbon 14 tagged thiocyanate ion. Unreacted thiocyanate was removed to give a solution containing only the halo- and thiocyanatodiazonium ions, chloride and electrically neutral decomposition products. In some experiments the amount of radioactivity in these neutral products was determined by scintillation counting of a toluene extract at this stage. The apparent first-order rate constants divided by the diazonium ion concentration for the formation of these neutral decomposition products are referred to as the second-order constants, k_d. The diazonium salts were converted in good yield to the corresponding chloro compounds by reaction with cuprous chloride. These were extracted into toluene and counted in this solution, and gave the total amount of thiocyanate introduced into the molecule which ultimately became toluene soluble. Since most of the measurements were made without the prior extraction to determine k_d, the products counted include both chlorophenyl thiocyanate and the neutral decomposition products. The resulting apparent first-order constants, divided by the di-

(1) Paper IV is E. S. Lewis and H. Suhr, *Chem. Ber.*, **93**, in press (1960).

(2) A. Hantzsch and B. Hirsch, *Ber.*, **29**, 947 (1896).

(3) B. Hirsch, *ibid.*, **31**, 1253 (1898).

(4) A. Hantzsch, *et al.*, (a) *ibid.*, **30**, 2334 (1897); (b) **33**, 505 (1900); (c) **36**, 2069 (1903).

(5) K. H. Saunders, "The Aromatic Diazo Compounds," Edward Arnold & Co., London, 1949, pp. 117–125.

(6) J. F. Bunnett and R. E. Zahler, *Chem. Revs.*, **49**, 273 (1951).

(7) E. S. Lewis and M. D. Johnson, THIS JOURNAL, **81**, 2007 (1959).

(8) B. O. Bolto, M. Liveris and J. Miller, *J. Chem. Soc.*, 750 (1956).

(9) R. E. Parker and E. S. Lewis, unpublished observations.

(10) P. T. Austin and F. S. Smith, THIS JOURNAL, **8**, 89 (1886).

(11) F. Challenger and A. D. Collins, *J. Chem. Soc.*, **125**, 1377 (1924).