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A New Rearrangement Reaction of Azoxybenzene with Arenesulfonyl Chloride

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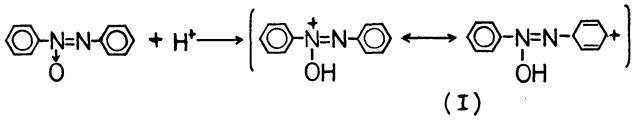
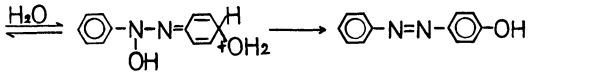
Azoxybenzene was found to react with arenesulfonyl chloride to afford *o*- or *p*-arenesulfonyloxyazobenzene. This new rearrangement reaction is found in various substituted azoxybenzenes and arenesulfonyl chlorides. By the use of the ^{18}O tracer technique, the *ortho* rearrangement was found to proceed *via* an intramolecular path, while the rearrangement to the *para* position was intermolecular. The yields of the rearranged products were determined by the isotopic dilution technique, while the migratory aptitude was also determined by the use of azoxybenzene-1-^{14}C. It was found that the ratio of the sulfonyloxy migration to the phenyl ring attached to the azoxy side to that of the azo side is 1 to 2 for the *ortho* rearrangement. On the bases of these observations, the mechanism of this new rearrangement reaction is discussed.

Azoxybenzene is known to undergo Wallach rearrangement in strong acidic media, such as sulfuric,[1] chlorosulfonic,[2] and fluorosulfonic acids,[3] to afford *p*-hydroxy azobenzene, and the reaction has been shown by an ^{18}O tracer experiment[4] to be an acid-catalyzed[5] intermolecular rearrangement. The following two mechanisms have been suggested:[6]

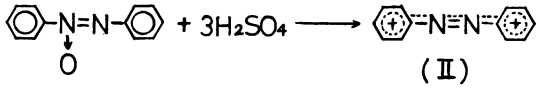


(I)



$$+H_2O + H^+ \quad (I)$$

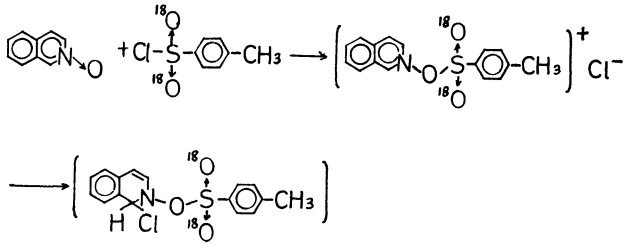
The former one is similar to that of the Bamberger reaction[7] and involves the initial formation of an intermediate (I), upon which subsequent nucleophilic attack by either water or a $-OSO_3H$ group takes place, while the other perhaps involves the symmetrical dication (II), in which both phenyl rings are liable to nucleophilic attack.



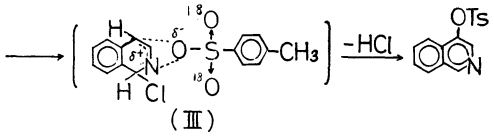
(II)

$$+H_3O^+ + 3HSO_4^- \quad (2)$$

Meanwhile, the reactions of pyridine and isoquinoline *N*-oxides with arenesulfonyl chloride are known to give 3-pyridyl and 4-isoquinolyl arenesulfonates, apparently *via* the oxygen-bridged ion-pair path[8] (III):

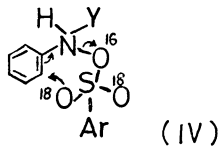


1) O. Wallach and L. Belli, *Ber*, **13**, 525 (1880).
2) V. O. Lukashevich and T. N. Kurdyumova, *Zh. Obshch, Khim.* **18**, 1963 (1948).
3) T. E. Stevens, *J. Org. Chem.*, **33**, 2667 (1968).
4) S. Oae, T. Fukumoto, and M. Yamagami, This Bulletin, **36**, 601 (1963).
5) M. M. Shemyakin, T. E. Agadzharyan, V. I. Maimind, and R. V. Kundryavtsen, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1963**, 1339.
6) H. J. Shine, "Aromatic Rearrangement," Elsevier Publ. Co., New York (1967), p. 275.
7) a) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd. Ed., Cornell Univ. Press, The George Bunta Company, Inc. (1969), p. 907; b) M. Murakami and Y. Yukawa, "Name Reaction in Organic Chemistry," (Jinmei-Yuki-Hannoshu), Vol. II, Asakura Book Publ. Co., Tokyo (1954), p. 228.
8) S. Oae, K. Ogino, S. Tamagaki, and S. Kozuka, *Tetrahedron*, **25**, 5761 (1969).



(III)

On the other hand, it has been suggested that the reaction of phenyl hydroxylamine with the same reagent to give *o*-hydroxy aniline proceeds through a concerted 6-membered cyclic process (IV).[9]



(IV)

In both cases, the initial step of the reaction is believed to be the sulfonylation of the *N*-oxide function. Therefore, it seemed that it would be interesting to use acylating agents, *e.g.*, acetic anhydride or arenesulfonyl chloride, for the study of the rearrangement of azoxybenzene, since, if the initial acylation proceeds successfully at the *N*-oxide function, then the subsequent rearrangement would proceed as in the similar rearrangement of a number of tertiary amine *N*-oxides with acylating agents. The Wallach reaction and the rearrangements of aromatic amine oxide with acylating agents have one common feature, *i.e.*, the generation of a cationic center in the course of the reaction. As in the Kuhara modification[10] of the Beckmann rearrangement of oximes the arenesulfonylation of the azoxy group may lead to an interesting modification of the Wallach rearrangement. Thus, we have investigated the title reaction and now wish to report a new rearrangement to afford *o*- and *p*-arenesulfonyloxyazobenzenes.

Results and Discussion

Unlike other aromatic and heteroaromatic oxides, the reaction of azoxybenzene with acetic anhydride[11] is sluggish and affords mainly reduced products, such as acetanilide and azobenzene. On the other hand, the reaction of azoxybenzene with arenesulfonyl chloride gave rearranged products, *i.e.*, *o*- and *p*-arenesulfonyloxyazobenzenes, along with arenesulfonic acid and hydrogen chloride. The reaction is also rather sluggish without a solvent, but proceeds smoothly in a polar solvent such as nitrobenzene. The results are summarized in Table 1. The yields of the products were determined by means of the isotopic dilution method using azoxybenzene-1-^{14}C.[12] The following five successive steps are conceivable for this rearrangement: (1) the sulfonylation of azoxy oxygen, (2) the nucleophilic attack of the chloride anion, (3) the

Table 1. The reaction of azoxybenzene-1-^{14}C with various sulfonyl chloride in nitrobenzene

Sulfonyl Chloride / Reaction Conditions	Products / Yield(%)	M.P.(°C)
O_2N-C$_6$H$_4$-SO_2Cl	C$_6$H$_5$-N=N-C$_6$H$_4$-OSO_2-C$_6$H$_4$-NO_2 (59.7)	144-6
110°C, 25hr	C$_6$H$_5$-N=N-C$_6$H$_4$-OSO_2-C$_6$H$_4$-NO_2 (24.8)	170-1
Br-C$_6$H$_4$-SO_2Cl	C$_6$H$_5$-N=N-C$_6$H$_4$-OSO_2-C$_6$H$_4$-Br (28.8)	100-1
110°C, 30hr	C$_6$H$_5$-N=N-C$_6$H$_4$-OSO_2-C$_6$H$_4$-Br (36.8)	175-6
CH_3-C$_6$H$_4$-SO_2Cl	C$_6$H$_5$-N=N-C$_6$H$_4$-OSO_2-C$_6$H$_4$-CH_3 (0.6)	85-6
110°C, 50hr	C$_6$H$_5$-N=N-C$_6$H$_4$-OSO_2-C$_6$H$_4$-CH_3 (61.4)	159-60
CH_3SO_2Cl	C$_6$H$_5$-N=N-C$_6$H$_4$-OSO_2CH_3 (63.8)	156-7
110°C, 50hr		

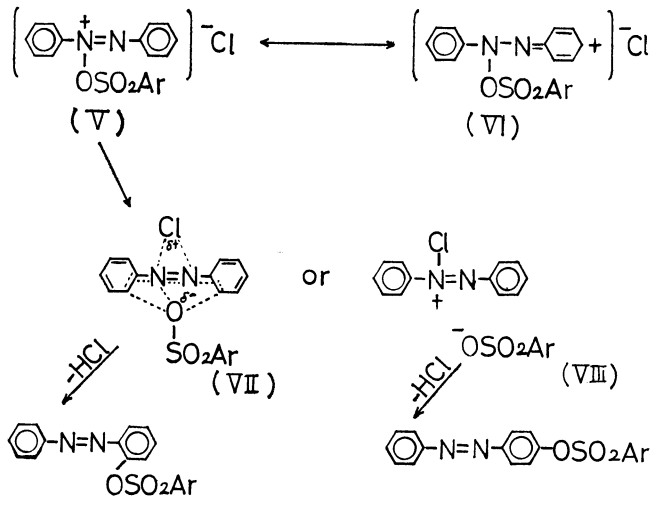
9) G. T. Tisue, M. Grassmann, and W. Lworuski, *ibid.*, **24**, 999 (1968).

10) M. Kuhara, K. Matsumiya, and N. Matsunami, *Mem. Coll. Sci. Univ. Kyoto*, **1**, 105 (1914); *Chem. Abstr.*, **9**, 1613 (1915).

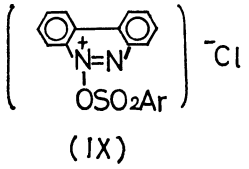
11) S. Oae, T. Maeda, and S. Kozuka, This Bulletin, **44**, 442 (1971).

12) L. C. Behr and E. C. Hendley, *J. Org. Chem.* **31**, 2715 (1966).

cleavage of the N–O bond, (4) the nucleophilic attack of the sulfonate group at either the *o*- or the *p*-position of either phenyl ring, and (5) the elimination of hydrogen chloride.



The formation of V is reasonable because, in the similar reaction of isoquinoline *N*-oxide with tosyl chloride, the formation of a similar *N*-tosyloxy salt was actually observed.[8] The nucleophilic attack of the chloride ion on the –N=N– group VII or VIII may be considered on the basis of the following evidence.

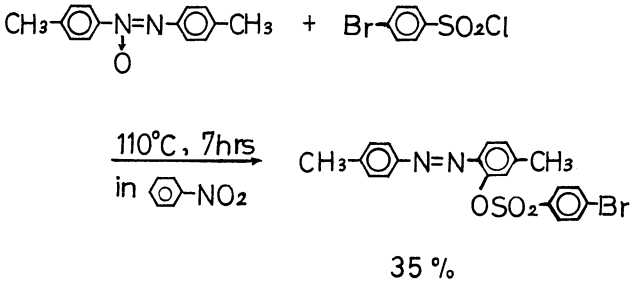


(IX)

i) In the reaction of sterically twisted benzocinnoline *N*-oxide with *p*-nitrobenzenesulfonyl chloride, no rearranged product was obtained because of the steric hindrance of the attack of the chloride ion on the azo group after the arenesulfonylation of the *N*-oxy function (IX).

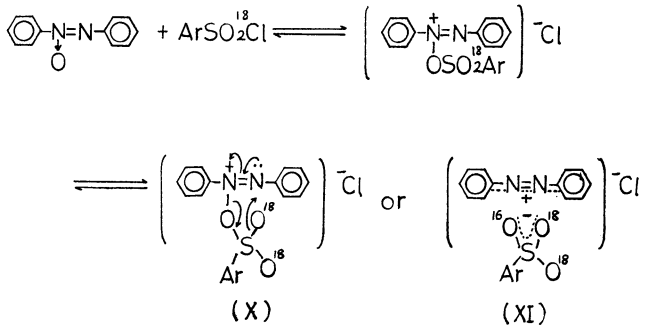
ii) If chloride ion attacks the *para* position of azoxybenzene, which is considered to be the most active site for nucleophilic attack,[13] *p*-chloroazobenzene could be found in the reaction of azoxybenzene with *p*-nitrobenzenesulfonyl chloride as in the reaction of quinoline *N*-oxide with tosyl chloride to give 4-chloroquinoline.[14] However, the results of the isotopic dilution analysis showed no formation of *p*-chloroazobenzene.

iii) When both *para* positions are blocked by substituents, as in the case of *p,p'*-dimethylazoxybenzene, the rearrangement to the *ortho* position occurs as is shown below:



Therefore, the attack of the chloride anion on the *para* position of VI does not seem as a prerequisite step for this rearrangement. Apparently the rearrangement proceeds easily with a better leaving *p*-nitrobenzenesulfonyloxy group, as in many other rearrangements involving electron-deficient centers. The data in Table 1 show that the ratio of the *ortho* migration to the *para* migration changes with the change in the *para* substituent on benzenesulfonyl chloride. That is, the rearrangement to the *ortho* position is predominant when the substituent is the nitro group. On the other hand, the rearrangement occurs mainly to *para*, accompanied by only a minor *ortho* rearrangement, when an electron-releasing methyl group is substituted. When the chloride ion approaches the azo group of V, a better leaving group, such as *p*-nitrobenzenesulfonate, would cleave heterolytically and migrate to the *ortho* position intramolecularly *via* the formation of the transition complex VII. In the case of *p*-methylbenzenesulfonate, which is a poor leaving group in comparison with *p*-nitrobenzenesulfonate, the chloride ion is added before the cleavage and VIII is formed prior to the rearrangement to the *para* position, since the *para* position of II is a much more electron-deficient site than the *ortho* position from the calculation of the electron density using the ω technique.[13] Our usual ^{18}O tracer experiments were carried out with ^{18}O-labelled *p*-substituted arenesulfonyl chloride: the findings on the ^{18}O distributions of the sulfonates, hydrolyzed products, *etc.* are tabulated in Table 2.

An inspection of the data reveals that the whole pattern of migration is very similar to that of the Wallach rearrangement. That is, *o*-brosyloxyazobenzene retains the original oxygen atom of azoxybenzene, implying an intramolecular oxygen-bridged ion-pair process for the *ortho* migration. On the other hand, all the oxygen atoms of *p*-brosyloxyazobenzene are completely scrambled, suggesting a solvent-separated ion-pair process or an intermolecular nucleophilic process for the *para* migration.



(X) (XI)

13) B. S. Thyagarajan, "Mechanism of Molecular Migrations," Vol. 1, John Wiley & Sons, Inc., New York (1968), p. 101.

14) M. Murakami and E. Matsumura, *Nippon Kagaku Zasshi*, **72**, 509 (1951).

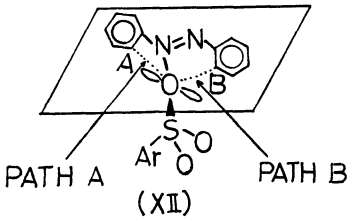
Table 2. ^{18}O Analytical results of the reacton of azoxybenzene with *p*-substituted arenesulfonyl chloride

Compounds	Excess atom% ^{18}O (calc.)
Br-C$_6$H$_4$-SO$_2$Cl	1.18
C$_6$H$_5$-N=N-C$_6$H$_4$-OSO$_2$-C$_6$H$_4$-Br	0.77 (0.79)
C$_6$H$_5$-N=N-C$_6$H$_3$(OH)	0.17
C$_6$H$_5$-N=N-C$_6$H$_4$-OSO$_2$-C$_6$H$_4$-Br	0.79 (0.79)
C$_6$H$_5$-N=N-C$_6$H$_4$-OH	0.79
Br-C$_6$H$_4$-SO$_3$H (as thiuronium salt)	0.82
C$_6$H$_5$-N(→O)=N-C$_6$H$_5$ (recovered)	0.14
O$_2$N-C$_6$H$_4$-SO$_2$Cl	0.68
C$_6$H$_5$-N=N-C$_6$H$_4$-OSO$_2$-C$_6$H$_4$-NO$_2$	0.52 (0.54)
C$_6$H$_5$-N=N-C$_6$H$_3$(OH)	0.28

Table 3. The counting data of the photolysis of azoxybenzene-1-^{14}C

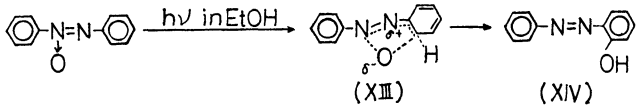
Substance	Activity
C$_6$H$_5$-N(→O)=N-C$_6$H$_5$	3.08×10^5 dpm/m mole
C$_6$H$_5$-NHCO-C$_6$H$_5$	3.84×10^4 "
C$_6$H$_3$(NH$_2$)(OH)	2.77×10^5 "

The small excess of ^{18}O found in the recovered azoxybenzene seems to suggest that there is a pre-equilibration of oxygen atoms between the azoxybenzene and arenesulfonyl groups prior to the rearrangement *via* either X or XI, though to a very minor extent; this is probably responsible for the small incorporation of ^{18}O in the *o*-hydroxyazobenzene obtained.



(XII)

Meanwhile, another interesting point of this rearrangement is that the sulfonyloxy group migrates to the two phenyl rings attached to the *N*-oxide group and the azo nitrogen, *i.e.*, in an intermediate XII for the *ortho* rearrangement. (Path A or Path B). The scheme involving the four-membered oxygen-bridged intermediate (Path A) resembles the intermediate of the isoquinoline rearrangement III. On the other hand, the photochemical rearrangement of azoxybenzene is known to proceed intramolecularly through a five-membered oxygen-bridged path, like Path B, as is be described below.



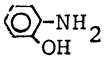
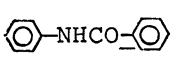
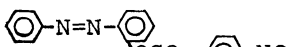
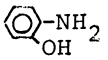
(XIII) (XIV)

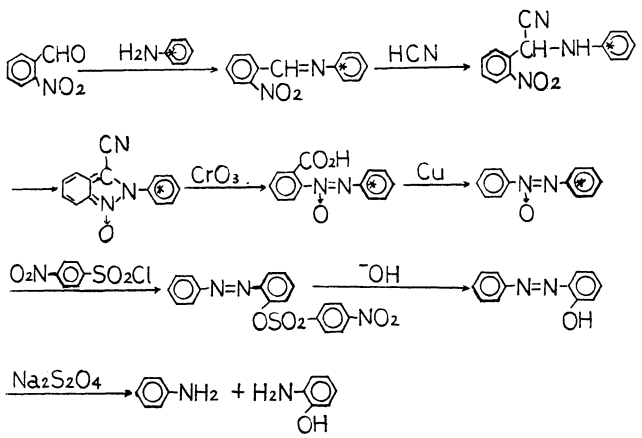
To shed further light on the mechanism, the reaction was carried out with azoxybenzene-1-^{14}C, and the location of the C-14 was determined by the reductive cleavage of *o*-hydroxyazobenzene XIV with sodium hydrosulfite to *o*-aminophenol and aniline. Aniline was converted to benzanilide, which was then subjected to the usual ^{14}C-activity measurements.

The data in Table 3 reveal that the photochemical rearrangement leads to no significant delocalization of the isotopic ^{14}C during the *ortho* rearrangement. However, there was a definite, though small, scrambling, and the ratio of Path A to Path B in an intermediate XII was found to be 13:87. This result shows that the main pathway for the photo rearrangement of azoxybenzene involves an intermediate XIII. Meanwhile, in the reaction of azoxybenzene-1-^{14}C with *p*-nitrobenzenesulfonyl chloride to afford *o*-(*p*-nitrobenzenesulfonyloxy)azobenzene, the ^{14}C distribution is somewhat different, as is shown in Table 4.

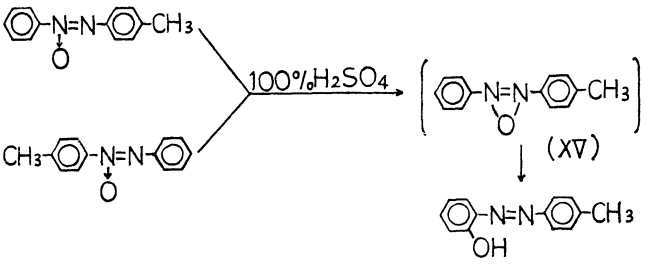
Incidentally, the synthesis of azoxybenzene-1-^{14}C and the degradation scheme are as is shown below:

TABLE 4. THE COUNTING DATA OF THE REACTION OF AZOXYBENZENE WITH *p*-NITROBENZENESULFONYL CHLORIDE FOR THE ORTHO REARRANGEMENT

Reaction condition	Activity of Compouns	
(1) 110°C, 30hrs		1.18×10^5 dpm/m mole
		7.67×10^4 "
		3.92×10^4 "
(2) 140°C, 20hrs		1.10×10^5 "
		6.62×10^4 "
		3.62×10^4 "



Earlier, Hahn and Jaffé[15] reported that the Wallach rearrangement of both α- and β-isomers of 4-methyl-azoxybenzene yields 2-hydroxy-4'-methylazobenzene as the sole rearrangement product. They suggested that



the initial step of this rearrangement is the formation of a common intermediate, probably 3-membered NNO ring XV. In this new rearrangement with arenesulfonyl chloride, the formation of a symmetrical 3-membered ring is quite unlikely since the migratory aptitude did not change with the variation of the reaction conditions, as is shown in Table 4. These data reveal that two-thirds of the migration of the sulfonyloxy group proceeds *via* Path B, while one third proceed A through Path A. The mode of the migration of the sulfonyloxy group in this reaction is similar to that in the photolysis of azoxybenzene.[16] A plausible model for the migration of the sulfonylation to azoxybenzene is illustrated by XII. The azoxybenzene molecule is plannar, and the sulfonyl group approaches the plane of azoxybenzene in a nearly perpendicular direction. Thus, one of the two *p* orbitals of the azoxy oxygen can lie parallel in the plane of azoxybenzene. To rearrange to the *ortho* position intramolecularly, it is necessary for the lone pair of azoxy oxygen to overlap with the *p*-orbitals of the *ortho* carbon atom in the phenyl ring. Therefore, the freedom of rotation around the C–N bond is necessary for the rearrangement to the *ortho* position. Meanwhile, the distance between the oxygen atom and the *ortho* carbon atom (A) in XII is longer than that between the oxygen atom and the other *ortho* carbon (B). Perhaps these factors are at least in part responsible for the facile rearrangement at the *ortho* position through Path B.

Although, a somewhat greater scrambling of ^{14}C was observed in the case of the *para* rearrangement of the sulfonyloxy group, there is a tendency similar to that of the *ortho* rearrangement, as is shown in Table 5. The data in Tables 4 and 5 reveal an unequal distribution of ^{14}C. These data imply that the presence of a symmetrical intermediate like dication II or a 3-membered NNO ring XV, as was seen in Wallach rearrangement, is unlikely in the course of sulfonyloxy migration for either the *ortho* or *para* position. On the basis of the ^{18}O and ^{14}C tracer experimental data, perhaps such intermediates XII and VIII are conceivable for the *ortho* and the *para* rearrangements respectively.

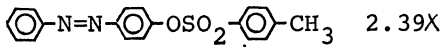
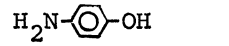
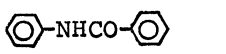
Experimental

Materials. *p*-Bromobenzenesulfonyl chloride (mp 75—76°C from ligroin) was obtained by the chlorosulfonylation of

15) C-S Hahn and H. H. Jaffé, *J. Amer. Chem. Soc.*, **84**, 946 (1962).

16) G. M. Badger and R. G. Buttery, *J. Chem. Soc.*, **1954**, 2243.

Table 5. The counting data of the reaction of azoxybenzene with tosyl chloride for para rearrangement

Reaction Conditions	Activity of Compouns	
110°C, 50hrs		2.39×10^5 dpm/m mole
		1.40×10^5 "
		9.03×10^4 "

bromobenzene with chlorosulfonic acid. *p*-Nitrobenzenesulfonyl chloride (mp 76—77°C from ligroin) was prepared by the oxidative chlorination of *p,p'*-dinitrodiphenyldisulfide in nitric and hydrochloric acids through bubbling with Cl_2 at 65°C. Benzo[*c*]cinnoline-1-oxide (mp 137—138°C from aq. ethanol) was synthesized from 2-nitro-2-aminobiphenyl and 1N methanolic sodium hydroxide. 4,4'-Dimethylazoxybenzene (mp 69—71°C from ethanol) was synthesized by the reduction of *p*-nitrotoluene with methanolic sodium hydroxide. ^{18}O-Labeled *p*-bromobenzenesulfonyl chloride was synthesized from *p*-bromothiophenol and ^{18}O-labeled water in dry chloroform by bubbling Cl_2 through at 0°C. ^{18}O-Labeled *p*-nitrobenzenesulfonyl chloride was synthesized similarly.

Azoxybenzene-1-^{14}C was prepared by the condensation of *o*-nitrobenzaldehyde with aniline-1-^{14}C in four steps according to the process reported by Behr.[12] Aniline-1-^{14}C was synthesized, starting from barium carbonate-^{14}C, through seven steps. The synthetic method was described previously.[17]

The Reaction of Azoxybenzene with Arenesulfonyl Chloride. A typical run was carried out as follows. Azoxybenzene and an excess of *p*-nitrobenzenesulfonyl chloride were mixed in nitrobenzene as solvents. The mixture was then heated at 110°C for 25 hr. After the reaction was completed, the nitrobenzene was steam-distilled. The residue was dissolved in methylene chloride, washed with water, dried with sodium sulfate, and chromatographed through an active alumina column, using methylene chloride as the eluent. The *o*- and *p*-(*p*-nitrobenzenesulfonyloxy)azobenzene were separated by recrystallization. These compounds were identified by a comparison of their properties with those of the authentic samples which were synthesized by reacting *o*- or *p*-hydroxyazobenzene with *p*-nitrobenzenesulfonyl chloride in pyridine. The yield was determined by the isotopic dilution technique. The other reactions were carried out similarly.

Isotopic Dilution Method. A typical run was carried out as follows. A mixture of azoxybenzene-1-^{14}C (0.10720 g) and *p*-toluenesulfonyl chloride (0.5 g) in nitrobenzene (2.0 m*l*) was heated at 110°C for 50 hr. After the reaction was completed, authentic samples of *o*-(*p*-toluenesulfonyloxy)azobenzene (0.09190 g) and *p*-(*p*-toluenesulfonyloxy)azobenzene (0.05486 g) were added to the reaction mixture. After the nitrobenzene had been removed by steam distillation, the residue was chromatographed and recrystallized from ethanol. Thus, *o*-(*p*-toluenesulfonyloxy)azobenzene (1.50×10^5 dpm/mmol) and *p*-(*p*-toluenesulfonyloxy)azobenzene (1.76×10^4 dpm/mmol) were separated. The recrystallization was continued until the specific radioactivity was settled. The ratio of the products was determined by calculation with the following equation:

$$W_x = \frac{W_1}{\left(\frac{S_0}{S_2}-1\right)}$$

where W_x: the weight of the desired substance
W_1: the weight of the added authentic substance
S_0: specific activity of the desired substance
S_2: specific activity of the separated substance

The results are given in Table 1.

Measurement of ^{14}C Activity. All the compounds were counted with a liquid scintillation counter (TEN) in a toluene solution, using POPOP as the scintillator.

The Reaction of 4,4'-Dimethyl Azoxybenzene with p-*Bromobenzenesulfonyl Chloride.* A mixture of 4,4'-dimethylazoxybenzene (0.80 g) and *p*-bromobenzenesulfonyl chloride (1.0 g) was heated in nitrobenzene at 110°C for seven hours. 2-(*p*-Bromobenzenesulfonyloxy)-4,4'-dimethylazobenzene (mp 139—140°C from ethanol: 0.54 g) was obtained by the procedure described above. This compound was identified by comparison with the authentic sample synthesized by reacting 2-hydroxy 4,4'-dimethylazobenzene with *p*-bromobenzenesulfonyl chloride in pyridine.

^{18}O-Tracer Study. The reactions of azoxybenzene with ^{18}O-labeled *p*-bromobenzenesulfonyl and *p*-nitrobenzenesulfonyl chlorides were carried out and the ^{18}O analysis was carried out in the usual way.[18] A typical run was as follows. A mixture of azoxybenzene (3.0 g) and ^{18}O-labeled *p*-bromobenzenesulfonyl chloride (4.0 g) in nitrobenzene (30 m*l*) was heated at 110°C for 30 hr. 2-(*p*-Brosyloxy)azobenzene (mp 100—101°C, 1.0 g) and 4-(*p*-brosyloxy)azobenzene (mp 175—176°C, 1.5 g) were then obtained by usual work-up, and a 0.4 g portion of the azoxybenzene recovered was subjected to ^{18}O analysis. The hydrolysis of 4-(*p*-brosyloxy)azobenzene (1.2 g) was carried out under refluxing in 20 m*l* of 20% sodium hydroxide for 5 hr. Then the solution was acidified with 10% HCl and extracted with ether. After the removal of the solvent, recrystallization from benzene gave 4-hydroxyazobenzene (mp 152—154°C, 0.3 g). The aqueous layer was carefully neutralized with Na_2CO_3, using phenolphthalein as the indicator. Then, a 10% EtOH solution of *s*-benzylisothiuronium salt (0.4 g) was added to the neutral solution. The precipitate thus formed was collected and recrystallized from ethanol. This crystal (mp 174—176°C 0.3 g) were identified as the thiuronium salt of *p*-bromobenzenesulfonic acid by comparing it with the authentic sample. 2-(*p*-Brosyloxy)-azobenzene was hydrolyzed similarly. The ^{18}O-analytical results of these esters and the hydrolyzed compounds are listed in Table 2.

Degradation of o-(p-*Nitrobenzenesulfonyloxy)azobenzene*-x-^{14}C. A mixture of the title compound (1.0 g) in 10 m*l* of ethanol and 2 m*l* of water was subjected to alkaline hydrolysis with

17) S. Oae, N. Furukawa, M. Kise, and M. Kawanishi, This Bulletin, **39**, 1212 (1966).

18) S. Oae, T. Kitao, and Y. Kitaoka, *Tetrahedron*, **19**, 827 (1964).

5.0 g of sodium hydroxide under reflux for five hours. After the reaction has subsided, the reaction mixture was poured into ice cold water and filtered. The filtrate was acidified with 10% hydrochloric acid and extracted with ether. After the evaporation of the ether, crude *o*-hydroxyazobenzene was obtained and recrystallized from ethanol (mp 81—82°C): 0.3 g of the pure compound was thus obtained. Into a mixture of 0.205 g of *o*-hydroxyazobenzene (0.001 mol) and 0.53 g of sodium hydrosulfite (0.003 mol) in 2 m*l* of water, 0.24 g of sodium hydroxide (0.006 mol) was added. The solution was then heated at 80°C for eight hours until the red color of *o*-hydroxyazobenzene disappeared. After the reaction, two times as much water was added to the reaction mixture and the solution was extracted with ether. Then, 0.05 g of benzoyl chloride was added to the ether solution. After heating on a hot plate, the ether was evaporated and the residue was recrystallized from ethanol to obtain benzanilide (mp 161—163°C, 0.034 g) After acidification with 10% hydrochloric acid, the water layer was made weakly alkaline with sodium carbonate and extracted with ether. After the subsequent evaporation of the ether, crude *o*-aminophenol was recrystallized with ethanol (mp 172—174°C) to obtain 0.043 g of the pure sample. The degradation of *p*-(*p*-toluenesulfonyloxy)-azobenzene was carried out similarly.

Photochemical Rearrangement of Azoxybenzene-1-^{14}*C.* A mixture of 0.544 g of azoxybenzene-1-^{14}C in 200 m*l* of ethanol was irradiated for 48 hr using a high-pressure mercury arc lamp at 20—25°C. After the condensation of the reaction mixture, it was poured into an alkaline solution, *i.e.*, 3 g of sodium hydroxide in 200 m*l* of water, and filtered under reduced pressure. The filtrate was acidified with 10% hydrochloric acid and extracted with ether. After the evaporation of the ether, crude *o*-hydroxyazobenzene was recrystallized from ethanol. The degradation of the ^{14}C-labeled *o*-hydroxyazobenzene to aniline and *o*-aminophenol was done by the procedure used previously.