Table V. Properties of Pyridinium S-Aryl Thiosulfates

$ArSSO_3^-$ $C_5H_5NH^+$ Ar =	Mp, °C	Formula	Calcd, % C	Calcd, % H	Found, % C	Found, % H
p-$CH_3C_6H_4$	115–117	$C_{12}H_{13}NO_3S_2$	50.86	4.62	50.80	4.72
p-ClC_6H_4	123–124	$C_{11}H_{10}ClNO_3S_2$	43.49	3.32	43.18	3.41
p-BrC_6H_4	129	$C_{11}H_{10}BrNO_3S_2$	37.94	2.89	37.91	3.01
p-$(CH_3)_3CC_6H_4$	139	$C_{15}H_{19}NO_3S_2$	55.36	5.88	54.94	5.87
p-$O_2NC_6H_4$	155–156	$C_{11}H_{10}N_2O_5S_2$	42.03	3.21	41.83	3.23

distilled water. The wash water was collected. Evaporation of the wash water under reduced pressure yielded pure sodium S-phenyl thiosulfate as its monohydrate, mp 180–182° dec. *Anal.* Calcd for $C_6H_5S_2O_3Na \cdot H_2O$: C, 31.30; H, 3.06. Found: C, 31.26; H, 3.33.

Sodium S-(*m*-nitrophenyl) thiosulfate was prepared by the method of Lecher and Hardy.[4b] This involves the reaction of bis(3-nitrophenyl) disulfide with sodium bisulfite. The only modification that was made in their procedures was to wash the final product a number of times with anhydrous methanol instead of only once.

Sodium S-Ethyl Thiosulfate. This was prepared as described in an earlier paper.[12]

Sodium S-benzyl thiosulfate was synthesized by the method of Milligan and Swan.[28]

***p*-Nitrothiophenol** was prepared by the procedure of Price and Stacy.[29] All the other aromatic thiols required for preparation of the various pyridinium S-aryl thiosulfates were purchased from commercial sources.

Solvents. Dioxane was purified by the same method used in the accompanying paper.[6b]

Procedure for Kinetic Runs. All runs except those involving the ethyl Bunte salt were carried out in the same type of reaction vessel used for kinetic studies of the hydrolysis of sodium aryl sulfates.[6b] The procedure for preparing and deaerating the reaction solutions was also the same as that employed in the sulfate studies. The course of the reactions was followed by removing aliquots at appropriate time intervals and titrating the mercaptan which had been produced by hydrolysis of the Bunte salt with 0.1 *N* iodine solution. After 10 half-lives an infinity mercaptan titer was determined, and the first-order rate constant for the run was determined from a plot of log $\{1 - [(RSH)/(RSH)_\infty]\}$ *vs.* time. The infinity mercaptan titer in each case corresponded satisfactorily to that expected from the amount of Bunte salt taken and the stoichiometry of eq 1.

In the case of the nitro-substituted S-aryl thiosulfates it was difficult to detect the end pont of the titration visually. With these compounds the end point was detected potentiometrically using a Beckman Model 72 pH meter with a combined platinum–calomel Beckman electrode.[30]

The runs with the ethyl Bunte salt in either water or deuterium oxide were carried out using a previously described procedure.[12] The runs with the same Bunte salt in 60% dioxane were carried out in sealed tubes. These tubes, containing aliquots of the reaction solution, were degassed in the usual manner before being sealed. The reaction was followed by removing tubes at appropriate time intervals, cooling and opening them, and then titrating the contents for mercaptan in the usual way with 0.1 *N* iodine solution.

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(28) B. Milligan and J. M. Swan, *J. Chem. Soc.*, 2172 (1962).

(29) C. C. Price and G. W. Stacy, *J. Am. Chem. Soc.*, **68**, 498 (1946).

(30) L. Gringas and G. Sjostedt, *Acta Chem. Scand.*, **15**, 433 (1961).

Orientation, Reactivity, and Mechanism in the Addition of Methanol to 4-Chlorobenzyne[1]

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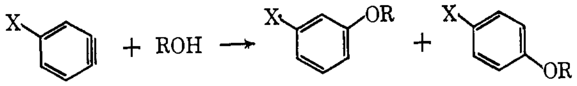
Contribution from the Department of Chemistry, Brown University, Providence, Rhode Island 02912. *Received July 5, 1966*

Abstract: 4-Chlorobenzyne adds methanol to form *p*- and *m*-chloroanisole in different ratios depending on the sodium methoxide concentration. The observed *para/meta* ratio is between 4.2 and 6.3 in neutral methanol and between 1.8 and 2.6 in 2 *M* methanolic sodium methoxide. The change in ratio shows that methoxide ion is more reactive than methanol toward 4-chlorobenzyne. The greater reactivity of methoxide ion and the fact that a stronger orienting effect prevails in methanol than in methoxide addition indicate that methanol addition is stepwise rather than a concerted, four-center process.

An aryne generated in an alcoholic solvent usually adds the alcohol to form an aryl alkyl ether.[3–5] Addition of alcohol to a 4-substituted benzyne leads to a mixture of isomeric ethers of *meta* and *para* orientation.



We have generated 4-chlorobenzyne in methanol solution by several routes, both in the presence and in the absence of sodium methoxide, and we have found

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[1] Financial support by the National Science Foundation is gratefully acknowledged.

[2] University of California, Santa Cruz, Calif. 95060.

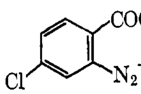
[3] M. Stiles, R. G. Miller, and U. Burckardt, *J. Am. Chem. Soc.*, **85**, 1792 (1963).

[4] G. Wittig and R. W. Hoffmann, *Chem. Ber.*, **95**, 2718, 2729 (1962).

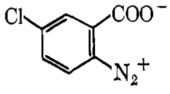
[5] R. W. Hoffmann, G. E. Vargas-Nunez, G. Guhn, and W. Sieber, *ibid.*, **98**, 2074 (1965).

that the *para/meta* isomer ratio varies with the sodium methoxide concentration.

5- and 4-chlorobenzenediazonium-2-carboxylates (**1** and **2**, respectively) were prepared from the corresponding chloroanthranilic acids.[3,6] On being refluxed in methanol, these zwitterionic intermediates decomposed to form chloroanisoles in *para/meta* ratios of 4.2 and 4.8, respectively. These compare with *para/meta* ratios averaging 4.1 observed by Hoffmann, *et al.*,[5] for addition of ethanol to 4-chlorobenzyne.



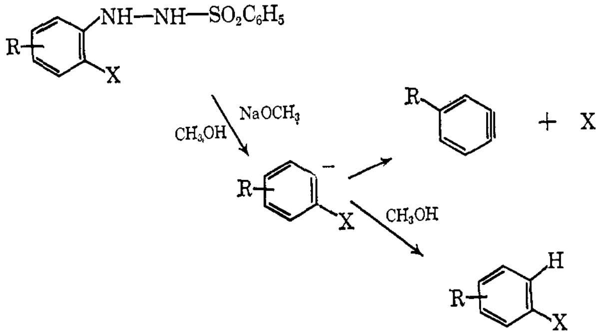
1

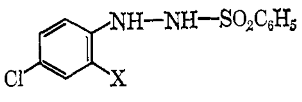


2

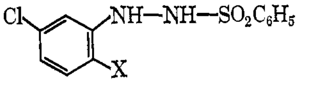
From the decomposition of **1** in a 2 *M* solution of sodium perchlorate in methanol, the two chloroanisoles were obtained in a *para/meta* ratio of 4.4. It is evident that salt effects on the orientation of methanol addition to 4-chlorobenzyne are negligible.

The reactions of 1-(*o*-haloaryl)-2-benzenesulfonhydrazides with sodium methoxide in methanol produce *o*-halophenyl anions with a negative charge on the carbon that originally carried the hydrazido group.[7-9] Such anions may either capture a proton from the solvent, forming a halobenzene, or lose halide ion to give an aryne and thence an anisole derivative. In the case of 1-(*o*-chlorophenyl)-2-benzenesulfonhydrazide reacting with sodium methoxide in methanol-O-*d* solution, chlorobenzene containing more than 0.95 deuterium atom per molecule is formed irrespective of whether sodium methoxide is in large excess (2 *M*) or furnished only in stoichiometric amount.[9] This shows that *o*-halophenyl anions are intermediates at all methoxide concentrations.





3a, X = Br
b, X = I

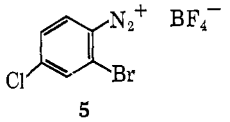


4a, X = Br
b, X = I

From reactions of isomeric bromohydrazides **3a** and **4a** with methanolic methoxide, isomeric aryl bromides, but the same aryne, are expected. The actual reactions with 1 molar equiv of methoxide afforded the expected bromochlorobenzenes in 84% yield plus 1–2% of chloroanisoles. Although the chloroanisole yields were low, precise determination of *para/meta* ratios was possible by gas–liquid chromatography. The *para/meta* ratios observed were 5.1 from **3a** and 6.3 from **4a**. These are similar to the ratios from decomposition of **1** and **2** in methanol.

However, **3a** and **4a** gave very different *para/meta* chloroanisole ratios on reaction with 2 *M* sodium methoxide in methanol. The ratios observed were 1.9 from **3a** and 2.5 from **4a**.

The reactions of isomeric diazonium salts **5** and **6** with sodium methoxide were also investigated. The principal products on reaction of *o*-halobenzenediazonium ions with methanolic methoxide are halobenzenes in which hydrogen has taken the place of the diazonium group. In other studies, it has been shown that when only 1 equiv of methoxide is used per mole of diazonium salt, reaction occurs by a radical mechanism.[9,10] In contrast, reaction with 2 *M* sodium methoxide (a large excess) occurs *via* *o*-halophenyl anion intermediates.



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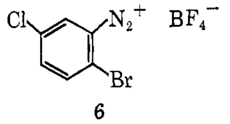

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Accordingly it is not surprising that **5** and **6** gave only traces of chloroanisoles on reaction with a stoichiometric amount of sodium methoxide; measurement of the *para/meta* ratio was not feasible. It is also not surprising that reaction with 2 *M* sodium methoxide afforded the two chloroanisoles in yields about the same as from **3a** and **4a**, respectively. Moreover, the *para/meta* ratios were about the same: 1.8 from **5** and 2.6 from **6**.

The reactions of iodohydrazides **3b** and **4b** with sodium methoxide were more convenient to study than those of the corresponding bromohydrazides because *o*-iodophenyl anions give a larger fraction of aryne in partitioning between proton capture and halide ion loss. However, they were attended by a new complication, deiodination of the chloroiodobenzenes to chlorobenzene and iodide ion. This complication is not fully understood; it is now under further study in this laboratory by Mr. Carl C. Wamser. Deiodination is observable on treatment of *m*-chloroiodobenzene with 1-phenyl-2-benzenesulfonhydrazide in methanolic sodium methoxide. We believe that deiodination occurs after removal of the hydrazide group, but, whether after or before, it does not affect the partitioning of 4-chlorobenzyne between *m*- and *p*-chloroanisole.

From reaction of **4b** with 1 molar equiv of sodium methoxide, the chloroanisoles were obtained in a *para/meta* ratio of 4.7. But with 2 *M* sodium methoxide, the chloroanisole *para/meta* ratio was 2.6. Again the sharp contrast between the ratios at high and low methoxide concentration is evident.

Iodohydrazide **3b** was exposed to a series of sodium methoxide solutions of varying concentration. The *para/meta* chloroanisole ratio varied from 5.6 with

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(6) F. M. Logullo and L. Friedman, personal communication; *cf.* L. Friedman and F. M. Logullo, *J. Am. Chem. Soc.*, **85**, 1549 (1963).

(7) R. W. Hoffmann, *Chem. Ber.*, **98**, 222 (1965).

(8) J. F. Bunnett and D. A. R. Happer, *J. Org. Chem.*, **31**, 2369 (1966).

(9) H. Takayama, unpublished experiments.

(10) J. F. Bunnett, D. A. R. Happer, and H. Takayama, *Chem. Commun.*, 367 (1966).

Table I. Reactions of 4-Chlorobenzyne Precursors in Methanol

			Chloroanisoles				
Precursor	[$NaOCH_3$], *M*	Temp, °C	*meta*, %	*para*, %	*para*/*meta*	Dihalobenzene, %	Other products, %
1	Nil	Reflux	3.9	16.3	4.2	. . .	*p*-ClC_6H_4COOH, 42
	a	Reflux	*b*	*b*	4.4	. . .	*p*-ClC_6H_4COOH, 23
2	Nil	Reflux	*c*	*c*	4.8	. . .	Not determined
3a	0.1	50–55	0.3	1.4	5.1	83.8	Br^-, 2.9
	2.0	50–55	1.1	2.0	1.9	91.7	Br^-, 4.3
4a	0.1	50–55	0.14	0.86	6.3	84.1	Br^-, 1.4
	2.0	50–55	0.37	0.93	2.5	89.3	Br^-, 2.1
3b	0.07	61	1.51	8.46	5.6	69.1	C_6H_5Cl, 2.9; I^-, 15.3
	0.14	61	1.86	9.31	5.0	75.5	C_6H_5Cl, 2.4; I^-, 15.8
	0.27	61	3.21	9.80	3.0	77.1	C_6H_5Cl, 2.8; I^-, 19.4
	1.1	61	4.75	11.6	2.4	68.5	C_6H_5Cl, 7.1; I^-, 25.5
	2.2	61	5.1	9.0	1.8	50.3	C_6H_5Cl, 31; I^-, 42.2
4b	0.1	44.3	0.35	1.66	4.7	29.6	C_6H_5Cl, 1.7
	2.1	44.3	0.50	1.30	2.6	18.8	C_6H_5Cl, 21.2
5	0.1	*d*	*e*	*e*	*e*	87.2	
	2.0	*d*	0.86	1.54	1.8	90.7	Br^-, 3.1
6	0.1	*d*	*e*	*e*	*e*	85.3	
	2.0	*d*	0.33	0.87	2.6	93.2	Br^-, 1.2

[a] $NaClO_4$, 2.0 *M*. [b] Total chloroanisole yield <5%, but not precisely determined. [c] Not determined. [d] Reaction commenced at room temperature, completed at 50–55°. Traces of chloroanisoles formed; *para*/*meta* ratio not determinable.

very dilute methoxide through intermediate values to 1.8 in 2.2 *M* sodium methoxide.

The results of all the foregoing experiments are summarized in Table I.

Discussion

In the experiments described above, 4-chlorobenzyne has been generated from eight precursors, comprising four isomeric pairs. From the pairs **3a**–**4a** and **3b**–**4b**, it was possible to observe the *para*/*meta* chloroanisole isomer ratio at both high (2 *M*) and low sodium methoxide concentrations. From the pair **1**–**2**, 4-chlorobenzyne could be generated and the *para*/*meta* chloroanisole ratio could be observed only in the absence of sodium methoxide, since in its presence "deamination" occurs forming chlorobenzoic acids. From the pair **5**–**6**, the chloroanisole isomer ratio could be measured only at high sodium methoxide ion concentration because mere traces of chloroanisoles are produced when but 1 equiv of methoxide is furnished per mole of **5** or **6**.

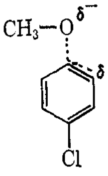
Chloroanisole *para*/*meta* ratios between 4.2 and 6.3 were observed in the absence of sodium methoxide or at very low methoxide concentrations. *para*/*meta* ratios between 1.8 and 2.6 were measured at high (2 *M*) methoxide concentrations, and in the case of **3b** intermediate ratios were observed at intermediate base concentrations. Throughout, these ratios were substantially independent of the constitution of the 4-chlorobenzyne precursor.

The fact that nearly the same *para*/*meta* ratio was obtained from decomposition of **1** in 2 *M* sodium perchlorate in methanol as in the pure solvent shows that the dependence of isomer ratio on sodium methoxide concentration does not represent a salt effect.

Relative Reactivity of Nucleophiles. The change in the *para*/*meta* ratio with increase in sodium methoxide concentration demonstrates that methoxide ion is more reactive than methanol toward 4-chlorobenzyne. Were it equally or less reactive, no appreciable change in isomer ratio would have been observed. Even in 2 *M* sodium methoxide, the molar concentration of methanol is some 12-fold greater than that of methoxide ion.

In contrast, Mack and Huisgen[11] concluded that piperidine and lithium piperidide in ether solution are almost equally reactive toward 9-phenanthryne. This conclusion was based on experiments of a different sort than ours. Though it is remarkable that an anionic nucleophile and its conjugate acid should be nearly equal in reactivity in one case and very different in another, these conclusions are not necessarily contradictory because they pertain to different systems.

The Transition States for Addition. The predominance of *p*- over *m*-chloroanisole in methoxide ion addition (or rather, methoxide-catalyzed methanol addition) to 4-chlorobenzyne may be comprehended with reference to transition states **7** and **8**. Each transition state has partial negative charge on oxygen and partial negative charge on carbon. Thus, each has partial phenyl anion character. It is known that



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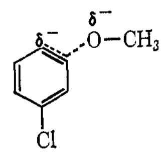

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halogen substituents accelerate the attack of bases on *meta* hydrogens more than on *para* hydrogens,[12,13] and thus that *meta* exceed *para* halogens in their stabilizing effect on phenyl anions. Accordingly, the chlorine stabilizes transition state **7** more than **8**, and predominantly *p*-chloroanisole is formed on protonation (by the solvent) of the phenyl anions resulting from methoxide addition.

An alternative mechanism for methoxide-catalyzed addition would involve proton donation to carbon (by solvent molecules) concerted with attachment of methoxide oxygen to carbon. The transition state

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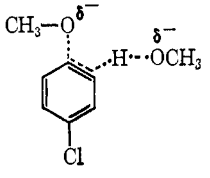
(11) W. Mack and R. Huisgen, *Chem. Ber.*, **93**, 608 (1960).

(12) G. E. Hall, R. Piccolini, and J. D. Roberts, *J. Am. Chem. Soc.*, **77**, 4540 (1955).

(13) R. Huisgen, W. Mack, K. Herbig, N. Ott, and E. Anneser, *Chem. Ber.*, **93**, 412 (1960).

would be depicted as **9**.[14] Because of the orientation effect, proton donation to carbon would lag behind C–O bond formation.

This possibility can virtually be rejected by an extended application of the principle of microscopic reversibility. Concerted addition *via* **9** would require that formation of 4-chlorobenzyne from attack of methoxide ion on *p*-chloroanisole be concerted, *i.e.*, that the methoxy group should depart from carbon (as methoxide ion) as the hydrogen was removed. That reaction is not known, but it is known that anisole can be *ortho* metalated by *n*-butyllithium and that *o*-methoxyphenyllithium is stable toward loss of its methoxy group.[15] Also, base-catalyzed hydrogen isotope exchange can be effected *ortho* to halogen substituents,[12,16] which are better leaving groups than methoxy. It is therefore extremely improbable that methoxide-induced elimination of methanol from *p*-chloroanisole or methoxide-catalyzed addition of methanol to 4-chlorobenzyne is concerted.



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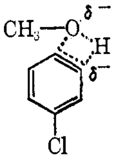


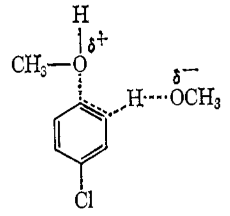
10

For the neutral addition of methanol to 4-chlorobenzyne, three mechanisms require consideration. One is a concerted, four-center addition *via* transition state **10**.[14] Such a mechanism has been advocated by Huisgen[17] for addition of piperidine to arynes, and by other workers[3,18] for addition of alcohols and carboxylic acids. However these authors do not consider attachment of the proton and the nucleophilic residue to carbon to be fully synchronous. Bond-making between nitrogen or oxygen and carbon is assumed to have progressed farther than between hydrogen and carbon. This assumption was necessary in order to account for the marked orienting effects of polar substituents.

One of the principal grounds for proposing concerted, four-center addition was experimental evidence that piperidine and lithium piperidide are almost equally reactive with arynes.[11] But methanol is much less reactive than sodium methoxide with arynes, and ethanol is much less reactive than chloride, bromide, and iodide ions.[4] The four-center mechanism would supposedly have a special advantage in the avoidance of charged intermediates, but that advantage is not manifest in the reactivity of alcohols with arynes.

Indeed, our observation that the orienting effect of chlorine is stronger for methanol addition under neutral conditions than with methoxide catalysis implies that there is *more* negative charge on carbon in the transition state for neutral addition. The genesis of the orienting effect is stabilization of negative charge on carbon. Greater negative charge on carbon is difficult to rationalize if **10** is the transition state for methanol addition, since **10** has acidic and basic sites juxtaposed in such a way as to neutralize each other as the reaction occurs. Admittedly a highly nonsynchronous concerted addition might have pronounced dipolar character in the transition state. However, if the C–H bond is but slightly formed in the transition state, its bond energy may not be sufficient to offset the considerable angle strain of **10**. Thus the concerted, four-center mechanism does not give a good account of the facts.

Termolecular concerted addition *via* a transition state such as **11**[14] is conceivable. The advantage of this mechanism would presumably be that it avoids the accumulation of negative charge on carbon in the transition state. But this advantage is not evident in the rather low reactivity of alcohols with arynes. Also, the orienting effect of chlorine indicates considerable negative charge on carbon in the transition state.



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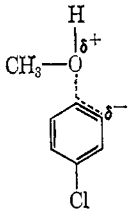

12

The transition state for the first and probably rate-limiting step of stepwise addition of methanol may be visualized as **12**.[14] The first dipolar intermediate would then undergo intra- or intermolecular proton shift to form the final adduct. This mechanism would not predict high reactivity for methanol, and high reactivity is not observed. With a weak nucleophile such as methanol, the transition state would be expected to be attained later on the reaction coordinate than with a strong nucleophile such as methoxide ion.[19] Accordingly there should be more negative charge on carbon in the transition state and stronger orientation by chlorine, as observed.

Thus the stepwise mechanism for addition of methanol gives the most satisfactory account of the facts. Both the uncatalyzed and methoxide-catalyzed additions appear to be initiated by straightforward nucleophilic attack on carbon, and the less reactive nucleophile is the more selective.

Experimental Section

Materials. 5-Chlorobenzenediazonium-2-carboxylate (1). 2-Amino-4-chlorobenzoic acid was diazotized in absolute ethanol after Stiles, *et al.*,[3] and the hydrochloride of 1 was precipitated by addition of ether. The precipitate was collected, suspended in methanol, and titrated with 0.3 *M* methanolic sodium methoxide (external indicators in spot plate) until the mixture was basic to methyl red but acidic to phenolphthalein. A clear solution was obtained. Addition of ether precipitated 1 which was collected, washed with cold tetrahydrofuran, and transferred wet into methanol or 2 *M* methanolic sodium perchlorate. The yields of chloro-

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[14] For simplicity, only transition states leading to *p*-chloroanisole are shown.

[15] H. Gilman and J. W. Morton, Jr., *Org. Reactions*, **8**, 258 (1954); R. G. Jones and H. Gilman, *ibid.*, **6**, 339 (1951).

[16] J. A. Zoltewicz and J. F. Bunnett, *J. Am. Chem. Soc.*, **87**, 2640 (1965); J. Hine and P. B. Langford, *J. Org. Chem.*, **27**, 4149 (1962).

[17] R. Huisgen and J. Sauer, *Angew. Chem.*, **72**, 91 (1960); R. Huisgen, "Organometallic Chemistry," H. Zeiss, Ed., Reinhold Publishing Corp., New York, N. Y., 1960, p 79.

[18] G. Wittig, *Angew. Chem.*, **77**, 752 (1965); *Angew. Chem. Intern. Ed. Engl.*, **4**, 731 (1965).

[19] G. S. Hammond, *J. Am. Chem. Soc.*, **77**, 334 (1955); *cf.* R. A. Ogg, Jr., and M. Polanyi, *Trans. Faraday Soc.*, **31**, 1375 (1935).

anisoles listed in Table I are based on the weight of 2-amino-4-chlorobenzoic acid used.

4-Chlorobenzenediazonium-2-carboxylate (2). 2-Amino-5-chlorobenzoic acid was diazotized with isopentyl nitrite in tetrahydrofuran solution containing a catalytic amount of trichloroacetic acid, after Logullo and Friedman.[6] The resulting precipitate was collected, washed twice with methanol, and then transferred into methanol for reaction.

The preparation and properties of **3a** and **4a** have been described by Bunnett and Happer.[8]

1-(2-Iodo-4-chlorophenyl)-2-benzenesulfonhydrazide (3b) was prepared from 2-iodo-4-chloroaniline[20] by the method of Bunnett and Happer,[8] and purified by crystallization from benzene containing a trace of methanol. White needles formed, mp 154.5–155°.

Anal. Calcd for $C_{12}H_{10}ClIN_2O_2S$: C, 35.25; H, 2.45; halogen, 39.78. Found: C, 35.43; H, 2.59; halogen, 39.58.

1-(2-Iodo-5-chlorophenyl)-2-benzenesulfonhydrazide (4b). 2-Iodo-5-chloronitrobenzene[21] was reduced to 2-iodo-5-chloroaniline which was characterized as its acetyl derivative, mp 180–180.5°.

Anal. Calcd for C_8H_7ClINO: C, 32.49; H, 2.37; halogen, 54.99. Found: C, 32.61; H, 2.39; halogen, 54.92.

The aniline was converted to **4b**, white crystals from ether-pentane, mp 149.5–150.5°, analogously to the above.

Anal. Calcd for $C_{12}H_{10}ClIN_2O_2S$: C, 35.25; H, 2.45; I, 31.06. Found: C, 35.83; 35.86; H, 2.62, 2.92; I, 30.64.

Diazonium fluoroborates **5** and **6** were made by diazotization of the corresponding anilines in 37–40% fluoroboric acid in water, at *ca.* −5 to 0°. The precipitated diazonium salts were collected, washed with small portions of the chilled fluoroboric acid solution and ice-cold water, dissolved in acetone, and precipitated by addition of ether. The reprecipitated salts were colorless; they were collected and dried.

Anal. Calcd for **5**, $C_6H_3BBrClF_4N_2$: C, 23.60; H, 0.99. Found: C, 23.83, 23.53; H, 1.27, 1.17.

Anal. Calcd for **6**, $C_6H_3BBrClF_4N_2$: C, 23.60; H, 0.99. Found: C, 23.90, 23.86; H, 1.29, 1.35.

Procedure for Reactions and Analysis of Products. In a small round-bottom flask, a weighed quantity of a 4-chlorobenzyne precursor (usually 0.001 mole), weighed quantities of suitable comparison standards for purposes of analysis by gas-liquid chromatography, and a measured volume of a standard methanolic solution of sodium methoxide were combined. In the reactions with 0.1 *M* sodium methoxide, approximately 1 equiv of $NaOCH_3$ was furnished per mole of precursor. The comparison standards used included bromobenzene (with **3b** and **4b**), *p*-bromochlorobenzene and *o*-chloroanisole (with **3a** and **5a**), *m*-bromochlorobenzene and *o*-chloroanisole (with **4a** and **6**), and *o*-chloroanisole (with **1**). A reflux condenser was fitted to the flask. In the cases of **5** and **6**, the reaction solution was prepared at *ca.* −20°. No gas evolution was evident at that temperature, but gas evolution commenced as the solutions warmed to the vicinity of room temperature. In the other cases, gas evolution was not evident until the reaction mixtures were heated as noted in Table I.

On completion of heating, the reaction solution was poured into cold water and the resulting mixture was extracted with pentane or benzene. In several cases, as indicated in Table I, the water layer was acidified with nitric acid and diluted to standard volume, and aliquots of the diluted solution were titrated potentiometrically with silver nitrate for determination of halide ion. The pentane or benzene layer was dried over magnesium sulfate and analyzed by gas-liquid partition chromatography (10% Carbowax 20M on Chromosorb P columns). Molar response ratios were determined and the observed areas were corrected as necessary. In the cases of **1**, **3a**, **4a**, **5**, and **6**, chloroanisole yields were determined *vs.* *o*-chloroanisole as standard and bromochlorobenzene yields against the added isomeric bromochlorobenzene as standard.

For the most part peaks were identified by retention time analysis. From one reaction of **3b** with 2 *M* sodium methoxide, the two chloroanisole products were condensed from the effluent of a gas-liquid chromatography column. Their infrared spectra were identical with those of authentic samples of the relevant isomers.

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Stereochemistry of the Cycloaddition Reaction of 1,2-Bis(trifluoromethyl)-1,2-dicyanoethylene and Electron-Rich Alkenes[1]

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Abstract: 1,2-Bis(trifluoromethyl)-1,2-dicyanocyclobutanes are formed at room temperature by the cycloaddition of *cis*- and *trans*-1,2-bis(trifluoromethyl)-1,2-dicyanoethylene to electron-rich alkenes. Although the rate of cyclobutane formation is strongly influenced by solvent, comparative fluorine nmr studies establish that many of these cycloaddition reactions take place with high stereospecificity over a wide range of solvent polarity. The first examples of nonstereospecific cycloaddition reactions of this type are reported, and evidence is presented that these polar additions occur *via* an intermediate.

Cycloaddition reactions of alkene to alkene have generally been achieved either thermally or photochemically,[2] but it has been demonstrated that strongly electrophilic olefins may cycloadd to electron-rich alkenes under surprisingly mild conditions without the influence of light or heat. Thus, the strong π acid, tetracyanoethylene, forms 1,1,2,2-tetracyanocyclobutanes (I) exothermically with a variety of electron-rich alkenes at 0–30°.[3] In contrast, thermal cycloadditions undergone by simple alkenes, allenes, fluoroalkenes,

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