law. This absorption band is absent in the 1,4 cycloadduct and in 1,3-cyclopentadiene.

The equilibrium constant for the reaction between N-sulfinylbenzenesulfonamide and 1,3-cyclopentadiene was determined by preparing solutions of diene and dienophile of known initial concentrations, measuring the concentration of the N-sulfinyl derivative at equilibrium, and calculating the concentrations of diene and cycloadduct at equilibrium. This was done for three different sets of initial concentrations at four different temperatures, as summarized in Table I.

TABLE I

DETERMINATION OF THE EQUILIBRIUM CONSTANT OF THE REACTION BETWEEN N-SULFINYLBENZENESULFONAMIDE AND 1,3-CYCLOPENTADIENE IN DICHLOROMETHANE

Temp, ±0.1°C	Initial concn of N-sulfinyl-benzene-sulfonamide, moles/l. × 10^2	Initial concn of 1,3-cyclo-pentadiene, moles/l. × 10^2	Equil concn of 1,4-cyclo-adduct, moles/l. × 10^3	Equil const	Equil const, av
10	2.252	2.383	8.03	35.1	
10	2.163	2.217	7.31	35.2	35.9
10	1.820	2.000	6.19	37.3	
15	2.252	2.383	6.52	23.6	
15	2.163	2.217	5.87	23.0	23.8
15	1.820	2.000	4.95	24.8	
20	2.252	2.383	5.73	18.9	
20	2.163	2.217	5.14	18.3	18.8
20	1.820	2.000	4.24	19.3	
25	2.252	2.383	4.13	11.4	
25	2.163	2.217	3.63	10.9	11.2
25	1.820	2.000	2.95	11.3	

A plot of the logarithm of the average equilibrium constant *vs.* the inverse absolute temperature yielded a straight line. The standard heat of reaction was obtained from the slope of the straight line, using the Gibbs–Helmholtz equation, and was found to be −13.9 kcal. The standard free-energy change was found to be −1.4 kcal at 25°, and the standard entropy change was −41.9 eu, also at 25°.

These results are quite comparable to the thermodynamic parameters recently reported[6] for the corresponding 1,4-cycloaddition reaction between nitrosobenzene and 1,3-cyclopentadiene. For this reaction, $\Delta H^\circ = -14.8$ kcal and $\Delta S^\circ = -44.6$ eu at 25°. For both equilibria, the standard heats of reaction are somewhat lower than for "conventional" Diels–Alder reactions, such as the dimerization of 1,3-cyclopentadiene in either the gaseous or the condensed state.[7] On the other hand, the standard entropy change is somewhat higher.[7] Both parameters however seem to fall well within the general pattern of a 1,4-cycloaddition pattern.

Experimental Section

Materials.—1,3-Cyclopentadiene (bp 39–40°, n_D 1.4446) was prepared by pyrolytic depolymerization and distillation of the commercially available dicyclopentadiene at atmospheric pressure.[8] The purity of the monomer was ascertained by gas–liquid partition chromatography. The Perkin-Elmer Model 154 gas chromatograph was also used for this analysis with 20% QF-1 on Chromosorb P 30–60 mesh, column packing. The gas–liquid partition chromatographic analysis of the cyclopentadiene was carried out at two different column temperatures (~100 and ~180°) to ascertain the absence of impurities such as cyclopentane or polymerized cyclopentadiene. In each case a single peak was obtained.

N-Sulfinylbenzenesulfonamide was prepared by the reaction of benzenesulfonamide and thionylchloride in 20% yield, mp 70–71° (lit.[9] mp 70–71°).

Spectrograde quality dichloromethane was obtained from Eastmen Organic Chemicals.

Equilibrium Constant Measurements. Mechanics of Measurements.—A Beckman Model DB spectrophotometer was used for these studies. Volumes of the solutions were measured in a 1.0-cm silica cell (3-ml capacity) fitted with a ground-glass stopper. The spectrophotometer cell compartment was thermostated by means of circulating water jacket. Within the cell compartment temperature measurements were made with a calibrated thermometer. Observations of the temperature of the closed compartment over prolonged periods showed that temperature variation was less than ±0.1° at the temperatures employed (10, 15, 20, and 25°). A Mettler analytical balance was used for weighings and hypodermic syringes were employed to measure the small volumes of liquids.

Determination of the Equilibrium Constant.—Samples of conjugated diene, 1,3-cyclopentadiene, and N-sulfinylbenzenesulfonamide were accurately weighed into volumetric flasks and solutions were made up with the Spectrograde quality solvent dichloromethane. Plots of absorbances *vs.* concentrations were constructed for N-sulfinylbenzenesulfonamide at 412 mμ in dichloromethane at various temperatures. The concentrations of N-sulfinylbenzenesulfonamide employed were such that they obeyed the Beer–Lambert law. One-half hour before each run, the reactant solutions were placed in a water bath thermostated at the reaction temperature. At time zero, a 5.0-ml portion of the N-sulfinylbenzenesulfonamide solution was transferred by means of a syringe into 5.0 ml of 1,3-cyclopentadiene solution. Mixing was carried out in a flask (25-ml capacity) maintained at the reaction temperature. A portion (3 ml) of the reaction mixture was transferred by means of a hypodermic syringe into the cell and placed in the thermostated cell compartment, and the absorbance was measured after each 30 min till the absorbance was constant at equilibrium. Data have been summarized in Table I.

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N-Haloalkylamines. Analyses and Amination of Toluene[1]

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Although a number of different analytical procedures, *e.g.*, iodometry[6] and ultraviolet[7] and nmr spectroscopy,[6] have been used for analysis of N-halamines, this area has need for more thorough and systematic study. As examples of difficulties that have been encountered, one can cite the inability to obtain many of the members

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(6) P. Kovacic, C. T. Gorlaski, J. J. Hiller, Jr., J. A. Levisky, and R. M. Lange, *J. Am. Chem. Soc.*, **87**, 1262 (1965).

(7) F. W. Czech, R. J. Fuchs, and H. F. Antczak, *Anal. Chem.*, **33**, 705 (1961).

TABLE I

PREPARATION OF N-HALOALKYLAMINES[a]

Amine salt[b]	Water, moles	Hypohalite	Moles	Water, moles	N-Haloalkylamine
CH_3NH_3Cl	22.2	$Ca(OCl)_2$	1.2	30.2	CH_3NCl_2[c]
CH_3NH_3Cl	22.2	NaOBr[d]	2	55.5	CH_3NBr_2[c]
$(CH_3)_2CHNH_3OAc$[e]	21.1	$Ca(OCl)_2$	1.1	34.4	$(CH_3)_2CHNCl_2$[c]
$(CH_3)_3CNH_3OAc$[e]	21.1	$Ca(OCl)_2$	1.1	34.4	$(CH_3)_3CNCl_2$[c]
CH_3NH_3Cl	44.0	NaOCl	0.5		CH_3NHCl[f]
CH_3NH_3Cl	22.2	NaOBr[g]	0.5	13.9	CH_3NHBr[f]
$(CH_3)_3CNH_3Cl$	22.2	NaOCl	0.75		$(CH_3)_3CNHCl$[f]
$(CH_3)_2NH_2Cl$	22.2	NaOCl	1		$(CH_3)_2NCl$[f]
$(CH_3)_2NH_2Cl$	22.2	NaOBr[h]	1	27.8	$(CH_3)_2NBr$[f]

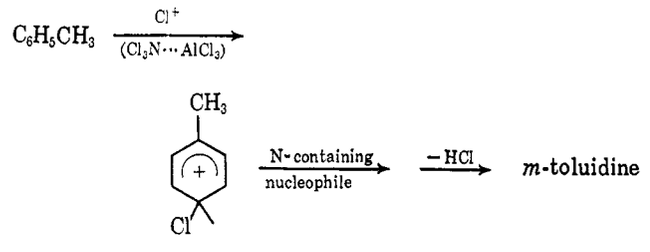
[a] See Experimental Section. [b] One mole. [c] The amine salt solution was added to the hypohalite solution. [d] $Br_2/NaOH/H_2O$ = 1/2.5/27.8 (molar). [e] The amine acetate salt was prepared by slowly adding the amine (1 mole) to acetic acid (1 mole), and then a mixture of sodium acetate (0.5 mole) and H_2O (21.1 moles) was added to buffer the solution. [f] The hypohalite solution was added to the amine salt solution. [g] $Br_2/NaOH/H_2O$ = 1/2.5/55.5 (molar). [h] $Br_2/NaOH/H_2O$ = 1/21/27.8 (molar).

in pure form because of decomposition, low solubility of certain ones in organic solvents of use in amination, and uncertainty concerning the data from iodometric determinations due to variation in the values with change in pH.[6]

Apparently, the earliest study on aromatic amination with N-halamines was by Lellmann and Geller who reported N-phenylpiperidine from the N-chloropiperidine–benzene–aluminum chloride reaction.[8] In 1960 Foote made the amazing observation that N-methyl-*m*-toluidine constituted the predominant basic product from treatment of toluene with N-chloromethylamine in the presence of aluminum chloride.[9] The unusual orientation has been the subject of subsequent studies with trichloramine.[6,10,11] A more detailed treatment of the prior literature is presented elsewhere.[6,10]

Results and Discussion

The N-haloalkylamines were prepared from the appropriate amine and hypohalite salts as described in Table I and the Experimental Section. Table II summarizes the elemental analyses and spectral studies; data for mono-, di-, and trichloramine are included for comparison. With the exception of N-bromomethylamine, there was excellent correlation between the theoretical and experimental values for the halogen/



nitrogen ratios. It appears that absorption in the 500–670-cm^{-1} region is characteristic of the N–Cl or N–Br structure. In comparison, C–Cl stretching absorption[12] occurs in the range 650–750 cm^{-1}. Multiple substitution of halogen on the same carbon usually leads to higher C–Cl frequencies.[12] Those N-haloalkylamines which possess the N–H functionality displayed bands at 3212–3306 cm^{-1}. The reported position[12] for stretching vibrations in secondary amines is 3310–3350 cm^{-1} and in secondary amides is 3310–3460 cm^{-1}.

TABLE II

ANALYSES OF N-HALOALKYLAMINES[a]

N-Haloalkylamine	X/N[b]	Ultraviolet[c] λ_{max}, mμ	Infrared,[d] cm^{-1}
$(CH_3)_2NCl$	0.99	275	1209, 1184, 1149, 1004, 912, 592
$(CH_3)_2NBr$	0.99	259, 319 (s)	1201, 1172, 1148, 1001, 900, 525
$(CH_3)_3CNCl_2$	2.01	259, 312 (s)	1480, 1460, 1400, 1370, 713, 595, 505
$(CH_3)_2CHNCl_2$	1.97	259, 312 (s)	1470, 1460, 1380, 1375, 704, 585, 520
CH_3NCl_2	1.85	259, 310 (s)	2990, 2955, 1450, 1440, 1410, 1126, 985, 648, 552
CH_3NBr_2	2.04	260	2970, 2920, 1450, 1440, 1405, 1119, 971, 581
$(CH_3)_3CNHCl$	0.96	264	3280, 3212, 668
CH_3NHCl	1.01	265	3306, 650, 620
CH_3NHBr	1.38	262	3300, 581, 538
NCl_3	3.17[e]	265, 345[e]	642
$NHCl_2$	2.02[f]	257, 300[e]	
NH_2Cl	1[g]	262[e]	

[a] The spectral determinations were made in carbon tetrachloride. [b] From iodometric and Kjeldahl analyses. [c] The literature contains the indicated λ_{max} values (mμ) (in aqueous solution): NCl_3, 340; $NHCl_2$, 297; NH_2Cl, 245; CH_3NHCl, 253; $(CH_3)_2NCl$, 263; CH_3NCl_2, 303 [W. S. Metcalf, *J. Chem. Soc.*, 148 (1942)]; and CH_3NHBr, 288; CH_3NBr_2, 236 [J. K. Johannesson, *Chem. Ind.* (London), 97 (1958)]. [d] Only selected bands are listed. [e] See ref 7. [f] R. M. Chapin, *J. Am. Chem. Soc.*, **51**, 2112 (1929). [g] G. H. Coleman and C. R. Hauser, *ibid.*, **50**, 1193 (1928).

The results from toluene aminations are summarized in Table III. In all cases the yields (0–9%) of the N-alkyltoluidines were lower than for trichloramine (42%).[6] Considerable evidence[6,10,11] has been obtained from the trichloramine investigations which points to a σ substitution (addition–elimination) mechanism.[6,10,11] For the most part this type of pathway would appear to pertain to the present studies. Several possible rationalizations come to mind in relation to the low yields: (1) destruction of N-haloalkylamine *via* intramolecular elimination of hydrogen halide or by homolytic decomposition, (2) adverse steric effect of the alkyl group, and (3) decreased availability of the more

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(10) P. Kovacic, J. A. Levisky, and C. T. Goralski, *ibid.*, **88**, 100 (1966).

(11) P. Kovacic and J. A. Levisky, *ibid.*, **88**, 1000 (1966); P. Kovacic and A. K. Harrison, unpublished work.

(12) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1962.

TABLE III

AMINATION OF TOLUENE WITH N-HALOALKYLAMINES

N-Haloalkylamine	Temp, °C	Basic product: Product	Isomer distribution: ortho	meta	para	Yield, %	Bp, °C (mm)
$(CH_3)_2NCl$	75	N,N-Dimethyltoluidine	4	88	8	4.8	68–78 (1.5)
$(CH_3)_2NBr$	75	N,N-Dimethyltoluidine	8	46	46	2.3	*a*
$(CH_3)_3CNCl_2$	50	N-*t*-Butyltoluidine	0	100	0	2.5	86–96 (2.5)
$(CH_3)_2CHNCl_2$	50	N-Isopropyltoluidine	0	100	0	6.2	78–84 (2.5)
CH_3NCl_2[b]	10	N-Methyltoluidine	3	91	6	2.3	*c*
CH_3NCl_2	50	N-Methyltoluidine	0	99	1	9.4	85–92 (6)
CH_3NCl_2	75	N-Methyltoluidine	0	100	0	8.5	*c*
$(CH_3)_3CNHCl$	75	N-*t*-Butyltoluidine	8	76	16	3.1	76–89 (2.5)
CH_3NHCl	75[d]	N-Methyltoluidine	0	100	0	1.6	98–105 (6)[e]

[a] The boiling point was approximately the same as for the product from $(CH_3)_2NCl$. [b] No amination occurred at −35°. [c] The boiling point was essentially the same as for the product formed at 50°. [d] Reaction was also studied at −35, 10, and 50°. [e] The product was apparently superheated.

basic nucleophile because of increased coordination with aluminum chloride.

Although most of the substituting species provided >87% of the *meta* isomer, exceptions were noted with N-bromodimethylamine and N-chloro-*t*-butylamine which produced appreciable amounts of the *ortho–para* isomers. Perhaps these two reagents participate in electrophilic[13] amination to some extent because of increased coordination of the catalyst on halogen. Ease of ionization in the order, $R_2N^{\delta+} > RNH^{\delta+} > NH_2^{\delta+}$, may also be a factor. Alternatively, the possibility of radical reactions being involved should be considered. In 1965, Bock and Kompa reported the formation of substituted N,N-dialkylanilines in 50–80% yield from N-chlorodialkylamines and toluene in the presence of diverse catalysts.[14] Fairly gross mixtures of the various isomers were observed. Working with N-chlorodimethylamine–toluene–ferrous sulfate, Minisci and co-workers found the orientation, *ortho/meta/para* = 9/53/38, for the N,N-dimethyltoluidine formed. These transformations[14,15] have been attributed[15] to the involvement of radical intermediates.

Several of the halamines failed to undergo the amination reaction with toluene, namely, N,N-dibromomethylamine, N-bromomethylamine, dibromamine, trifluoramine, and triiodamine. Studies on amination with dibromamine were frustrated by our inability to obtain a solution of the halamine in one of the standard aminating solvents. No aromatic amine was formed from the ethereal solution even when a large excess of aluminum chloride was used. Failure of amination in ether has been observed in the earlier work.[6]

Investigation of the neutral fractions from the N-haloalkylamine reactions (Table III) revealed the presence of the corresponding halotoluenes. Therefore, in those cases in which amination did not take place, apparently the intermediate complex eliminated a proton in total preference to combination with the nitrogen-containing nucleophile.

Experimental Section[16]

Materials.—Unless otherwise indicated, the reagents and authentic products were obtained commercially in high purity. Triiodamine was prepared according to the method of Chattaway and Orton[17] and dibromamine by modification[18] of a literature procedure.[19] Sodium hypobromite was generated by addition of bromine to sodium hydroxide solution at about 0°. Calcium hypochlorite was in the form of commercial HTH, and sodium hypochlorite as Purex or Clorox. The isomeric N-iospropyl- and N-*t*-butyltoluidines were synthesized as previously described.[20]

Preparation of N-Haloalkylamines.—The reactions[6] were carried out by slowly mixing a solution of the amine salt with hypohalite–water in the presence of toluene (9.4 moles) at about 0°. Stirring was continued for an additional 0.5 hr. The toluene solution was dried over sodium sulfate. No decomposition was observed at room temperature. Usually 0.3–0.5 mole of the N-halamine was prepared in approximately 500 ml of toluene, followed by dilution with toluene to the desired volume. Smaller quantities of dibromamine (0.04 mole) and triiodamine (0.025 mole) were employed because of the instability factor.

The halamine solutions for the spectral studies were prepared in carbon tetrachloride in the same manner.

Amination of Toluene with N-Haloalkylamines.—A toluene solution (865 ml) of the halamine (0.4 mole) was added slowly with stirring to a mixture of toluene (1.195 l.) and aluminum chloride (0.8 mole). After 1 additional hr, the reaction mixture was worked up as detailed earlier.[6] In some cases appreciable residue and high-boiling material, not identified, were also obtained from distillation.[21] Yields are based on an equimolar relationship between the halamine and aromatic amine.

Analytical Procedures.—A previous publication[6] describes the iodometric method for positive halogen and the Kjeldahl analysis for nitrogen.

A Perkin-Elmer 202 untraviolet spectrophotometer and Perkin-Elmer 337 infrared spectrophotometer were used. The infrared and ultraviolet studies were made in carbon tetrachloride. Isomer distributions for the N-alkyltoluidines were obtained by infrared spectroscopy involving comparisons with spectra of known mixtures of the authentic materials.

Acknowledgment.—We acknowledge support provided by the National Science Foundation.

(13) P. Kovacic, R. L. Russell, and R. P. Bennett, *J. Am. Chem. Soc.*, **86**, 1588 (1964); P. Kovacic, R. P. Bennett, and J. L. Foote, *ibid.*, **84**, 759 (1962).

(14) H. Bock and K. L. Kompa, *Angew. Chem. Intern. Ed. Engl.*, **4**, 783 (1965).

(15) F. Minisci, R. Galli, and M. Cecere, *Tetrahedron Letters*, **No. 51**, 4663 (1965).

(16) Boiling points are uncorrected.

(17) F. D. Chattaway and K. J. P. Orton, *Am. Chem. J.*, **23**, 363 (1900).

(18) The reaction product which contained ether, dibromamine, and ammonium bromide was poured into the calcium chloride solution. After being stirred for 45 sec, the dibromamine–ether solution was separated from the aqueous layer and maintained at −70°.

(19) G. H. Coleman and G. E. Goheen, *Inorg. Syn.*, **1**, 62 (1939).

(20) J. S. Buck and C. W. Ferry, "Organic Syntheses," Coll. Vol. II, A. H. Blatt, Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p 290.

(21) For example, dichloromethylamine (0.38 mole) with the appropriate amounts of aluminum chloride and toluene at 10° gave 1.2 g (bp 115–118° at 6 mm) of high-boiling product. At 75° no high-boiling fraction was produced.