(0.079 mole) was placed in a distillation flask equipped with a distillation head. The liquid was heated to reflux and a fraction boiling at 48–71° was removed over 7 hr. G.c. and the infrared spectrum indicated this to be the fluoroacetone ($\lambda_{\max}^{\text{film}}$ 5.55 μ) containing a small amount of isopropyl chloroacetate. The flask residue (0.8 g.) was identified as a mixture of isopropyl chloroacetate ($\lambda_{\max}^{\text{film}}$ 5.81 μ) and the undecomposed hemiketal ester in a 89:11 ratio, indicating that the decomposition had occurred to the extent of 89%. The flask temperature varied from 164 to 212°.

Decomposition of 1-Benzyloxy-1-(chlorodifluoromethyl)-2-chloro-2,2-difluoroethyl Acetate.—Ten grams (0.029 mole) of the above acetate was placed in a distillation flask equipped with a distillation head. The liquid was heated to reflux and a fraction boiling at 46–47° (4.5 g.) was removed periodically over a 0.5-hr. period, followed by a fraction boiling at 203–221° (4.5 g.) A residue (0.5 g.) was left in the flask. The flask temperature varied from 206 to 229° during the distillation. Examination by g.c. and infrared spectroscopy indicated that the first fraction was the fluoroacetone ($\lambda_{\max}^{\text{film}}$ 5.55 μ) and that the second fraction was 95% benzyl acetate ($\lambda_{\max}^{\text{film}}$ 5.73 μ). The residue consisted of benzyl acetate containing a trace of the hemiketal ester.

Decomposition of 1-(β-Phenylethoxy)-1-(chlorodifluoromethyl)-2-chloro-2,2-difluoroethyl Acetate.—Ten grams (0.0275 mole) of the above acetate was placed in a distillation flask equipped with a distillation head. The liquid was heated to reflux and a fraction boiling at 46–60° (4.7 g.) was collected in 0.5 hr. A second fraction boiling at 226–233° (4.0 g.) followed, leaving a residue of approximately 1 g. G.c. and infrared analyses indicated the first fraction to be the fluoroacetone ($\lambda_{\max}^{\text{film}}$ 5.55 μ) and the second fraction and residue to be β-phenethyl acetate ($\lambda_{\max}^{\text{film}}$ 5.75 μ) containing a small amount of the fluoroacetone. The flask temperature varied from 188 to 240° during the course of the decomposition.

Decomposition of 1-(*t*-Butoxy)-1-(chlorodifluoromethyl)-2-chloro-2,2-difluoroethyl Acetate.—Twenty grams (0.0635 mole) of the above acetate was placed in a distillation flask equipped with a distillation head. The liquid was heated to reflux (97°) and a distillate boiling at 50–67° was collected in 30 min. Refluxing stopped at this point and the flask temperature rose to 117° with no further distillation. The liquid remaining in the flask (3.6 g., theoretical 3.8 g.) was identified as acetic acid containing a small amount of the fluoroacetone. The distillate (11 g., theoretical 12.5 g.) was approximately 90% pure fluoroacetone. No *t*-butyl acetate was obtained.

In another decomposition experiment, the exit gas was passed through 50% H_2SO_4, and work-up of the solution gave some *t*-butyl alcohol, indicating isobutylene to be a decomposition product.

Examination of a 10-month-old sample of the hemiketal ester (stored at room temperature) indicated that extensive decomposition had taken place. Evaporation of the acetic acid from a portion of the sample (8.0 g., 0.025 mole) left 4.0 g. of a dark oil which solidified on standing. This was identified as the 2:1 reaction product of *sym*-dichlorotetrafluoroacetone and isobutylene, m.p. 81–93° (70%).

Anal. Calcd. for $C_{10}H_8Cl_4F_8O_2$: C, 26.4; H, 1.78. Found: C, 26.4; H, 2.08.

G.c. analysis resolved the crude product into two isomeric compounds (XIVa and XIVb) in a 35:65 ratio, and preparative gas chromatography (10% silicone rubber SE-30 on 60–80-mesh Diatoport W) separated the major isomer (XIVb): m.p. 72–74°; $\lambda_{\max}^{\text{Nujol}}$ 2.97 (OH), 6.00 (C=C), 8.60 (very broad, C–F) μ; n.m.r. (p.p.m. from TMS), singlet 2.08 ($-CH_3$), singlet 3.26 ($-CH_2-$), singlet 5.53 (vinyl proton).

Anal. Calcd. for $C_{10}H_8Cl_4F_8O_2$: C, 26.4; H, 1.78. Found: C, 26.2; H, 2.06.

Studies on Nitroso Compounds. II. Dimerization of 4-Substituted 2,6-Dichloronitrosobenzenes. An Equilibrium Controlled by the Resonance Effect of *para* Substituents[1]

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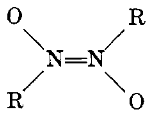
A previous report that *m*-trifluoromethylnitrosobenzene, unlike other nitroso compounds substituted in the *meta* or *para* positions only, is highly dimerized is shown to be in error. The compound reported as *m*-trifluoromethylnitrosobenzene is found to be *m*-trifluoromethylazoxybenzene. The true *m*-trifluoromethylnitrosobenzene gives no sign of dimer formation in solution. Spectrophotometric study of the monomer–dimer equilibrium in benzene of a series of 2,6-dichloro-4-X-nitrosobenzenes is reported. *para* substituents X were COOEt, H, CH_3, Cl, Br, and OCH_3. Electron-releasing substituents, including the halogens, favor dissociation to monomer. The change in $\Delta F°$ is proportional to the "resonance effect" of X. A comparison is made with benzaldehyde cyanohydrin equilibria and it is concluded that the "resonance effect" of *para*-X is nearly the same in nitrosobenzene as in benzaldehyde, with which it is isoelectronic.

It is well known that most C-nitroso compounds crystallize as colorless dimers, although the monomers, present in solution, are blue or green.[3-12] Both aromatic[9,10] and aliphatic[11,12] dimers have been shown by X-ray crystallography to have the azo dioxide structure A.[13]



A

It is also known[3-8] that substitution of groups larger than hydrogen in the *ortho* position of nitrosobenzene (particularly when both *ortho* positions are substituted) favors dimerization, and it has been shown[1] that the *ortho* effect is due to steric inhibition of resonance in the monomers.

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(1) Part I: R. R. Holmes, *J. Org. Chem.*, **29**, 3076 (1964).

(2) To whom correspondence should be sent.

(3) C. K. Ingold and H. A. Piggott, *J. Chem. Soc.*, **125**, 169 (1924).

(4) D. L. Hammick, *ibid.*, 3105 (1931).

(5) V. Keussler and W. Luttke, *Z. Elektrochem.*, **63**, 614 (1959).

(6) K. Nakamoto and R. E. Rundle, *J. Am. Chem. Soc.*, **78**, 1113 (1956).

(7) W. J. Mijs, S. E. Hoekstra, R. M. Ullmann, and E. Havinga, *Rec. trav. chim.*, **77**, 746 (1958).

(8) W. Luttke and B. G. Gowenlock, *Quart. Rev.* (London), **12**, 321 (1958).

(9) C. Darwin and D. Hodgkin, *Nature*, **166**, 827 (1950).

(10) C. P. Fenimore, *J. Am. Chem. Soc.*, **72**, 3226 (1950).

(11) M. Van Meersche and G. Germain, *Bull. soc. chim. Belges*, **68**, 244 (1959).

(12) H. Dietrich and D. C. Hodgkin, *J. Chem. Soc.*, 3686 (1961).

(13) Most dimers have the *trans* azo dioxide structure pictured, but some can also be prepared in a less stable form which is presumably the *cis* azo dioxide.

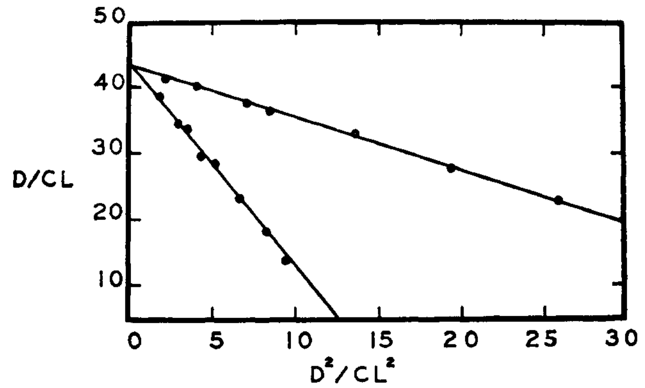

Figure 1.—Plots of *D/CL vs.* D^2/CL^2 from optical densities at 775 mμ and 25° for various concentrations in benzene of 2,6-dichloronitrosobenzene (lower line) and 2,6-dichloro-4-bromonitrosobenzene (upper line).

According to Hammick[4] nitrosobenzenes with *meta* or *para* substituents only are so little dimerized that one cannot tell from molecular weight studies whether the compounds are more dimerized or less than nitrosobenzene itself, which is[5,7] essentially 100% monomer in solution. It has been reported,[14] however, that *m*-trifluoromethylnitrosobenzene is highly dimerized even in the vapor phase, suggesting an unusual effect of the *m*-trifluoromethyl group. In order to investigate this unusual effect further, a quantity of *m*-trifluoromethylnitrosobenzene was prepared by oxidation of the corresponding amine with Caro's acid. A colorless solid melting at 73–74° and giving blue solutions in all solvents resulted. The same compound was obtained by dichromate oxidation of *m*-trifluoromethylphenylhydroxylamine. Analysis and molecular weight indicated the formula $C_7H_4F_3NO$, and infrared and ultraviolet spectra showed unequivocally that the substance was *m*-trifluoromethylnitrosobenzene. However, a substance melting at 48–49° was previously assigned[14] this structure, so that it was desirable to investigate further the compound melting at 48–49°. It has now been prepared by a standard method[15] for synthesis of azoxy compounds and shown by analysis, molecular weight, and infrared, ultraviolet, and n.m.r. spectra to be *trans-m*-trifluoromethylazoxybenzene.

Since the question of dimerization of *m*-trifluoromethylnitrosobenzene was raised in the earlier work[14] a spectrophotometric study of benzene solutions of the true *m*-trifluoromethylnitrosobenzene (m.p. 73–74°), following the characteristic monomer absorption peak at 753 mμ, was made. Beer's law was obeyed to better than 0.5% over the accessible range of concentrations (0.00625 to 0.25 *M*) at 25°. Therefore, under these conditions, the compound is essentially 100% monomer. It remains true, therefore, that a *meta* or *para* substituent by itself does not shift the monomer–dimer equilibrium enough to make practical a study of the electronic effect of substituents.

The present study was concerned with the effect of *para* substituents. It was necessary to study compounds which were also *ortho* substituted, since in the absence of this structural feature there is so little tendency to dimer formation that changes caused by *para* substitution cannot be detected. With all *ortho* positions occupied there is a considerable tendency to dimerize even in dilute solution, and the changes in equilibrium brought about by *para* substitution can easily be measured. A series of 2,6-dichloro-4-X-nitrosobenzenes was investigated, with X = COOEt, H, CH_3, Cl, Br, and OCH_3. The compounds were prepared by methods which have been described,[16] except for the 4-methoxy compound, which was made in two steps by direct chlorination of *p*-anisidine followed by Caro's acid oxidation of the amine. This route was much shorter than that followed by Hodgson and Wignall.[17] Although the product of chlorination of *p*-anisidine had the melting point reported[17] for 2,6-dichloro-4-methoxyaniline, it seemed advisable to supplement the evidence for this structure, partly because the earlier assignment used by Hodgson and Wignall[17] was not absolutely conclusive, and partly because direct dichlorination of *p*-anisidine has not been reported previously. Accordingly, the chlorinated amine was diazotized and deaminated to the known[18] 3,5-dichloroanisole, which showed that both chlorine atoms were indeed *ortho* to nitrogen in the amine.

The equilibria were followed spectrophotometrically, using the characteristic monomer absorption[5–7] at 750–800 mμ. If a simple monomer–dimer equilibrium is involved, if light absorption is due to monomer only, and, if Beer's law applies, then it can be shown that eq. 1 should hold where *D* is optically density, *C*

$$D/CL = -(D^2/CL^2)(2/K_c\epsilon_0) + \epsilon_0 \qquad (1)$$

is concentration of total nitroso compound (all figured as monomer) in moles per liter, ϵ_0 is the molar extinction coefficient per centimeter of cell length, *L* is length of cell in centimeters, and K_c is the equilibrium constant (in liters per mole) for reaction 2. According to eq. 1, a plot of *D/CL vs.* D^2/CL^2 should be linear.

$$\text{Ar–N}_2\text{O}_2\text{–Ar} \rightleftarrows 2\text{Ar–NO} \qquad (2)$$

The intercept gives ϵ_0 and K_c can then be calculated. Typical plots (from data obtained on benzene solutions of 2,6-dichloro-4-bromonitrosobenzene and 2,6-dichloronitrosobenzene at 25°) are given in Figure 1. Data on all the compounds studied gave similar straight lines, indicating that the conditions necessary in order for eq. 1 to hold were satisfied. Calculations based on these data gave equilibrium constants and standard free energy changes at 25° in benzene solution, recored in Table I, for the dimer dissociation reaction (eq. 2).

The fact that *p*-nitrosodimethylaniline,[6] *p*-iodonitrosobenzene,[6,19] and, under some conditions, *p*-nitrosoanisole[7] and *p*-bromonitrosobenzene[6] are monomeric even in the crystal, as shown by X-ray and spectroscopic evidence, suggests that electron-releasing substituents inhibit dimerization and that halogen may be electron-releasing, but no quantitative information has previously been available. The data in Table I confirm these qualitative ideas.

Column 4 of Table I lists the differences $\Delta F°$ (*para* X) − $\Delta F°$ (*para* H), which measure quantitatively the effect of a given *para* substituent on standard free energy changes for dissociation of the dimers. The

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[14] L. A. Errede and H. R. Davis, *J. Org. Chem.*, **28**, 1430 (1963).

[15] H. E. Bigelow and A. Palmer, "Organic Syntheses," Coll. Vol. II, R. Adams, Ed., John Wiley and Sons, Inc., New York, N. Y., 1943, p. 57.

[16] R. R. Holmes and R. P. Bayer, *J. Am. Chem. Soc.*, **82**, 3454 (1960).

[17] H. H. Hodgson and J. S. Wignall, *J. Chem. Soc.*, **130**, 2216 (1927).

[18] A. F. Holleman, *Rec. trav. chim.*, **40**, 461 (1921).

[19] M. S. Webster, *J. Chem. Soc.*, 2841 (1956).

TABLE I

EFFECT OF *para* SUBSTITUENTS ON EQUILIBRIUM CONSTANTS AND STANDARD FREE ENERGY CHANGES FOR DISSOCIATION OF 2,6-DICHLORO-4-X-NITROSOBENZENE DIMERS COMPARED WITH $\sigma_p{}^+ - \sigma_I$ AND WITH $\Delta F°_{p-X} - \Delta F°_{m-X}$ FOR BENZALDEHYDE CYANOHYDRIN EQUILIBRIA

para substituent X	$K_c \times 10^3$ moles/l.[a]	$\Delta F°$, kcal./mole	$\Delta\Delta F°$, kcal./mole[b]	$\sigma_p{}^+ - \sigma_I$	$\Delta F°_{p-X} - \Delta F°_{m-X}$ for ArCH(OH)CN
COOEt	1.13	2.64	+0.17	(+0.12)[c]	
H	1.5	2.48	−0.00	−0.00	
CH_3	3.9	1.91	−0.57	−0.25	−0.30
Cl	4.9	1.78	−0.70	−0.30	−0.32
Br	5.7	1.69	−0.79	−0.36	−0.39
OCH_3	52	0.39	−2.09	−1.01	−1.2

[a] In benzene solution at 25°. Reproducibility was ±10% in K_c and therefore ±0.06 kcal./mole in $\Delta F°$. [b] $\Delta F°$ for 2,6-dichloro-4-X-nitrosobenzene minus $\Delta F°$ for 2,6-dichloronitrosobenzene. [c] This value was obtained using σ_p rather than $\sigma_p{}^+$, but the difference is probably small, as with the nitro group.

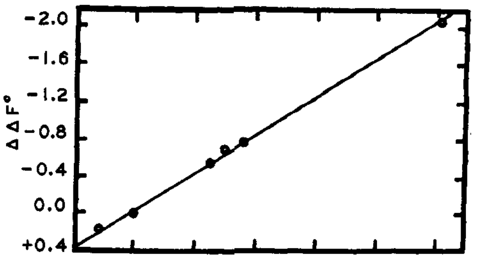
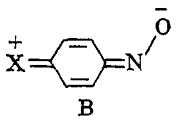


Figure 2.—Relationship between $\Delta F°_{p-X} - \Delta F°_{p-H}$ for dissociation of 2,6-dichloro-4-X-nitrosobenzene dimers and $\sigma_p{}^+ - \sigma_I$. *para* substituents X are COOEt, H, CH_3, Cl, Br, and OCH_3 from lower left to upper right on graph.

$\Delta\Delta F°$ values do not give a straight line when plotted against Hammett[20−22] σ or Brown[23,24] σ^+ constants. However, by plotting $\Delta\Delta F°$ values against $\sigma_p{}^+ - \sigma_I$, a good linear correlation was obtained, shown in Figure 2. The σ_I (inductive) constants are those of Taft and Lewis.[25] The difference ($\sigma_p - \sigma_I$) has been proposed by Taft[26] as a measure of the "pure" resonance effect of *para* substituents. In this case use of $\sigma_p{}^+$ is appropriate, no doubt because the nitroso group is strongly electron demanding.



B

If the data in Figure 2 are expressed in terms of a linear relationship between log K/K_0 and $[\sigma_p{}^+ - \sigma_I]$ as in the usual Hammett[20] ρ–σ treatment, a ρ value of −1.5 results, indicating[27] that dimer dissociation is indeed an electron-demanding reaction. The question of whether this electron demand is due to resonance among structures such as B in the monomer, after dissociation, or to some effect on the dimer as suggested by Luttke,[28] is an interesting one. X-Ray work[19] on *p*-iodonitrosobenzene shows that the aromatic monomers, if not *ortho* substituted, are planar, and also that the C–N bond joining the N═O group to the ring is shorter (1.3 Å.) than the similarly hybridized C–N bond (1.4 Å.) in *trans*-azobenzene.[29] It is apparently much shorter than the less conjugated C–N bond (1.5 Å.) in monomeric 10-bromo-2-chloro-2-nitrosocamphane.[30] Presumably the short bond is due to strong resonance interaction in *p*-iodonitrosobenzene (monomer). The C–N bond in dimeric aromatic nitroso compounds appears[9,10] to be about the same length (1.4 Å.) as in *trans*-azobenzene, indicating perhaps that resonance is less important in dimers.

From X-ray work[9] on *p*-bromonitrosobenzene it is known that dimers are nonplanar even if all *ortho* positions are occupied by hydrogen.[31] Among fully *ortho*-substituted compounds both dimers and monomers should be twisted out of plane, but the former are much more so. X-Ray data show[10] that in the crystal the dimer of 2,4,6-tribromonitrosobenzene has its rings twisted approximately 70° out of the plane of the central *trans*-N_2O_2 group. Although the angle of out-of-plane twist has not been determined experimentally for any *ortho*-substituted monomer, it is probably about the same as in di-*ortho*-substituted benzaldehydes and nitro compounds. In 2,6-dimethylbenzaldehyde this angle has been estimated spectroscopically[32] as 28–30°, and X-ray work on nitromesitylene[33] indicates a similar angle in that molecule.

Since resonance interaction is greater the closer a conjugated system is to planarity, resonance should be more important in monomers than dimers. If so, resonance interaction between *para* substituents and the nitroso group should also be greater in monomers than dimers, and the net resonance effect of *para* substituents should be proportional to, and in the same direction as, the effect on monomer stability.

Support for this idea may be found in a comparison of the nitroso equilibria with related benzaldehyde cyanohydrin equilibria.[34,35] Column 6 of Table I lists differences in $\Delta F°$ dissociation of benzaldehyde cyanohydrins with a given substituent X in *para* and *meta* positions. According to Ingold[36] this difference may be attributed to resonance interaction between the *para* substituent and the CH═O group of the aldehyde. According to Taft's quantitative treatment,[37] $\Delta F°_{p-X} - \Delta F°_{m-X}$ should be proportional to $\sigma_R{}^p - \sigma_R{}^m$. Examination of a list[38] of $\sigma_R{}^p$ and $\sigma_R{}^m$ values

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(20) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940.

(21) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).

(22) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1948).

(23) H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.*, **79**, 1913 (1957); *J. Org. Chem.*, **22**, 485 (1957).

(24) L. N. Ferguson, "The Modern Structural Theory of Organic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1963, pp. 415–417.

(25) R. W. Taft, Jr., and I. C. Lewis, *J. Am. Chem. Soc.*, **81**, 5343 (1959).

(26) R. W. Taft, Jr., N. C. Deno, and P. S. Skell, *Ann. Rev. Phys. Chem.*, **9**, 287 (1958).

(27) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, p. 574.

(28) W. Luttke, *Z. Elektrochem.*, **61**, 982 (1957).

(29) J. J. deLange, J. M. Robertson, and I. Woodward, *Proc. Royal Soc.* (London), **A171**, 398 (1939).

(30) J. M. Robertson, *et al.*, *J. Chem. Soc.*, 1976 (1961).

(31) If the dimer of *p*-bromonitrosobenzene were planar, the overlap of van der Waals radii between *ortho* H and an O atom from the other half of the dimer would be considerable.

(32) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962, p. 417.

(33) J. Trotter, *Acta Cryst.*, **12**, 173 (1959).

(34) J. W. Baker and H. B. Hopkins, *J. Chem. Soc.*, 1089 (1949).

(35) A. Lapworth and R. H. F. Manske, *ibid.*, 2533 (1928).

(36) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 678–680.

(37) Reference 27, pp. 594–597.

(38) Reference 24, p. 421.

shows that $\sigma_R{}^m = {}^1/_3\sigma_R{}^p$ to a good approximation, so that $\Delta F°_{p-X} - \Delta F°_{m-X}$ should be equal to a factor times ${}^2/_3\sigma_R{}^p$, *i.e.*, proportional to the pure resonance effect of *p*-X. In the benzaldehyde cyanhydrin equilibria $\sigma_p{}^+$ values are appropriate, as shown by the linearity of a plot of $\Delta F°_{p-X} - \Delta F°_{m-X}$ *vs.* $\sigma_p{}^+ - \sigma_I$.

On comparison of columns 4 and 6 of Table I, it is clear that the effect of a *para* substituent on $\Delta F°$ of nitroso dimer dissociation stands in a constant ratio of about 2:1 to the difference $\Delta F°_{p-X} - \Delta F°_{m-X}$ for cyanhydrin dissociation. The fact that this ratio is 2:1 might have been anticipated (because 1 mole of nitroso dimer produces 2 of monomer) if resonance interaction between X and N=O groups of the monomers and between X and CH=O groups of the corresponding isoelectronic benzaldehyde are virtually the same, an assumption confirmed by simple MO calculation. The observed 2:1 ratio would not be anticipated, however, unless the resonance effect of *p*-X is considerably less important in nitroso dimers than monomers.

Inductive effects of *para* substituents appear to have little influence on the nitroso equilibria, perhaps because inductive effects cancel between monomer and dimer. Dewar's recent work[39] indicating that "inductive" effects are really field effects suggests the possibility of such a cancellation. The dissociation of these nitroso dimers may, therefore, be the first example of an equilibrium controlled by the "pure" resonance effect of *para* substituents.

Experimental Section[40]

The spectrophotometric measurements were carried out as described previously[1] using a Beckman DU equipped with a double set of thermospacers through which water from a constant-temperature bath was circulated. A hole through the lid of the cell compartment allowed a thermometer to be placed so that its bulb was immediately adjacent to the cell containing solution. Solutions were used shortly after preparation, although little change in optical density was observed over 24-hr. periods. Matched 1.00-cm. silica cells (sometimes 0.100 cm.) were used and temperatures were maintained constant at 25.00 ± 0.05°. From replicate runs reproducibility of equilibrium constants was within about 10% which means that $\Delta F°$ values were reproducible to within ±0.06 kcal. The relevant properties of the nitrosobenzenes used follow: 2,6-Cl_2-4-COOEt, m.p. 154–155° (lit.[16] m.p. 154–155°), ϵ_0 39.3 (775 mμ); 2,6-Cl_2, m.p. 175–176° (lit.[16] m.p. 175.5–176°), ϵ_0 44.0 (775 mμ); 2,6-Cl_2-4-CH_3, m.p. 163–164° (lit.[16] m.p. 163–164.5°), ϵ_0 45.1 (775 mμ); 2,4,6-Cl_3, m.p. 144–145° (lit.[16] m.p. 145–146°), ϵ_0 43.6 (775 mμ); 2,6-Cl_2-4-Br, m.p. 144–145° (lit.[16] m.p. 144–145°), ϵ_0 43.6 (775 mμ); and 2,6-Cl_2-4-OCH_3, m.p. 127–128° (lit.[17] m.p. 126–127°), ϵ_0 54.0 (775 mμ).

***m*-Trifluoromethylnitrosobenzene.**—A solution of Caro's acid prepared from 108 g. (0.40 mole) of finely powdered potassium persulfate and 90 ml. (16.2 moles) of ice-cold, concentrated sulfuric acid was added to 600 g. of ice in a 3-l. beaker surrounded by an ice bath. Saturated aqueous sodium carbonate was added until the pH was 3 to 5, and then 30 ml. of glacial acetic acid was added. A solution of 16.8 g. (0.104 mole) of *m*-trifluoromethylaniline in water (600 ml.) and methanol (360 ml.) was added dropwise with vigorous stirring over a period of 2 to 3 hr. The yellow solid was removed, washed with water, and steam distilled to give blue vapor which condensed to blue liquid and finally white solid (16.3 g., 0.093 mole, 92%) melting at 71–73°. Recrystallization from absolute ethanol several times gave material melting at 73–74°.

Anal. Calcd. for $C_7H_4F_3NO$: C, 47.98; H, 2.30; F, 32.55; N, 8.00; mol. wt., 175. Found: C, 47.89; H, 2.43; F, 32.47; N, 7.87; mol. wt. (cryoscopic), 167, 176 (benzene), 171 (*p*-dichlorobenzene), 183, 205 (benzophenone).

***m*-Trifluoromethylazoxybenzene.**—Arsenic trioxide (22.6 g., 0.11 mole) was dissolved in a solution of 27.5 g. (0.69 mole) of sodium hydroxide in 60 ml. of water. To this solution was added 17.9 g. (0.0943 mole) of *m*-trifluoromethylnitrobenzene and 60 ml. of water. The mixture was stirred vigorously and refluxed for 27 hr. The oily product was removed and washed with cold, dilute hydrochloric acid, when it solidified. The crude, yellow-brown product (9.8 g., 55%) melted at 47°. Recrystallization from absolute ethanol gave pale yellow blades (6.2 g.) melting at 48–49°.

Anal. Calcd. for $C_{14}H_8F_6N_2O$: C, 50.31; H, 2.41; F, 34.11; N, 8.38; mol. wt., 334. Found: C, 50.38; H, 2.38; F, 33.97; N, 8.42; mol. wt. (cryoscopic), 340, 336 (naphthalene), 356 (acetic acid).

The infrared spectrum (CCl_4 and CS_2 solutions) of *m*-trifluoromethylnitrosobenzene showed the intense peak at 1500 cm.$^{-1}$ characteristic[41] of aromatic nitroso monomers, and the visible spectrum (ethanol, benzene) the low intensity band at 700–800 mμ also characteristic[6] of aromatic nitroso monomers. Both of these peaks were missing from spectra of solutions of *m*-trifluoromethylazoxybenzene. The ultraviolet spectrum of *m*-trifluoromethylnitrosobenzene in ethanol [λ_{max} 300 mμ, (ϵ_{max} 4000), 227 (8100), 267 (7300) (sh), and 218 (7700)] was practically identical with that of nitrosobenzene itself and its simple substitution products.[6,42,43] The ultraviolet spectrum of *trans*-*m*-trifluoromethylazoxybenzene was (see also ref. 14) practically identical with that of *trans*-azoxybenzene.[44]

The n.m.r. spectrum reported earlier[14] for the compound melting at 48–49° (*trans*-*m*-trifluoromethylazoxybenzene) was recorded on a Varian V-4300-2, 40 Mc./sec. This spectrum suggested a symmetrical structure. The compound was reexamined using a Varian A-60 which has better resolution, and the new spectrum was resolved into two separate areas of two peaks indicating clearly the presence of phenyl rings in different magnetic environments. The first area had major peaks at τ 1.43 and 1.59, and the second at τ 2.25 and 2.37.

In contrast to the n.m.r. spectrum of the azoxy compound, that of *m*-trifluoromethylnitrosobenzene was a continuum of peaks beginning at τ 1.77 and extending to τ 2.35. These peaks could not be separated easily into two areas as was possible with the azoxy compound, indicating but one type of phenyl ring in the nitroso compound, as expected for this structure.

2,6-Dichloro-4-methoxyaniline.—Dioxane (10 g.) was cooled in ice and saturated with chlorine, then a solution of 12.3 g. (0.1 mole) of *p*-anisidine in 20 g. of dioxane was added with stirring over a period of 20 min. During the addition chlorine was passed through the mixture. The precipitate which formed in the orange solution was removed and washed thoroughly with dioxane, then water. The solid was washed with dilute aqueous alkali and then recrystallized from hot ethanol (Norit) several times to remove a violet dye in the crude product. There was obtained 1.2 g. (6.2%) of white, crystalline material melting at 72–73° (lit.[17] m.p. 71°). It was found to be better to make several small runs rather than one large one. A sample of the compound was diazotized and deaminated with ethanol by the procedure given by Vogel[45] for tribromoaniline. After several crystallizations of the crude deamination product from ethanol, long white needles of 3,5-dichloroanisole melting at 39–40° (lit.[18] m.p. 39°) were obtained.

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[39] M. J. S. Dewar and Patrick J. Grisdale, *J. Am. Chem. Soc.*, **84**, 3548 (1962).

[40] Some of the analyses were by the Schwartzkopf Microanalytical Laboratories, Woodside, N. Y.

[41] W. Luttke, *Z. Elektrochem.*, **61**, 302 (1957).

[42] E. Hertel and F. Lebok, *Z. physik. Chem.* (Frankfurt), **B47**, 319 (1940).

[43] Y. Tsuzuki, T. Nemura, and N. Hirasawa, *Ber.*, **74**, 616 (1941).

[44] Reference 32, pp. 282–285, 431.

[45] A. I. Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green and Co., New York, N. Y., 1954, p. 589.