Reactions with 1,4-dichloro-2-butene (0.10 molar reaction) and with 1,3-dibromopropane (0.20 molar reaction) using the same solvent ratios and procedures as described for compound III, resulted in nondistillable residues.

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Amine Oxidations with Iodine Pentafluoride. Preparation of Azoisobutane[1]

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Several organic amines, and some related organic compounds, have been exposed to the mild fluorinating agent, iodine pentafluoride,[2] in methylene chloride or methylene chloride–pyridine solutions. The results of some of these experiments are summarized in Table I. Although most organic amines were observed to react vigorously when mixed with iodine pentafluoride, a controllable interaction occurred in the presence of the inert solvent. In the experiments reported in the table, hydrolysis of the reaction mixture was carried out before isolation of any products was attempted; hence, some of the materials isolated were formed by hydrolysis of uncharacterized intermediates.

The first five examples in the table illustrate the dehydrogenation of a primary amine containing an α-methylene group. With pyridine present in the reaction mixture it was possible to isolate the corresponding nitrile in 50–90% yield. Since the aldehyde accompanying the nitrile probably arises from hydrolysis of an imine (the product of

$$R—CH_2NH_2 \xrightarrow[(2)H_2O]{(1)IF_5} R—CN + RCHO$$

incomplete dehydrogenation), conditions better for this dehydrogenation than those given in the table may exist.[3]

t-Butylamine was oxidized readily to 2,2′-dimethyl-2,2′-azopropane (azoisobutane). This method of preparation of this interesting and useful azo compound appears to be quite superior to that reported.[4] However, vapor phase chromatography of the azoisobutane produced in the iodine pentafluoride oxidation indicated a very small amount of impurity that was not removed readily by washing and distillation. Chromatographic purification of samples might be required to obtain uncontaminated material.

Hydrazobenzene was oxidized readily to azobenzene. There was no sign of further reaction iodine pentafluoride and azobenzene; solutions of azobenzene in pure iodine pentafluoride were warmed to 100°, and the azobenzene was recovered unchanged upon hydrolysis of the iodine pentafluoride.

Although oxidation of dibenzylamine and tribenzylamine proceeded smoothly to produce benzaldehyde, oxidation of other secondary and tertiary amines, of primary amines containing an α-substituent, and of aromatic amines led mostly to uncharacterized, tarry products.

Oximes, when added to a methylene chloride solution of iodine pentafluoride, underwent a Beckmann rearrangement. The last three examples in the table illustrate this. Hydrolysis of unchanged oxime during the processing of the reaction mixture appeared to be the major side reaction, although some of the acetanilide produced in the acetophenone oxime rearrangement underwent aromatic iodination.

EXPERIMENTAL

Melting points and boiling points are uncorrected. Iodine pentafluoride was obtained from the Matheson Co.; it was pumped *in vacuo* from the cylinder, trapped in a Kel-F test tube at −78°, and allowed to melt in a stream of dry nitrogen. The test tube then was detached from the vacuum line and the iodine pentafluoride was withdrawn and measured in a glass pipet.

Reaction of iodine pentafluoride and amines. Not all of the amine reactions mentioned in the table are detailed here, but the methods and results are illustrated amply.

(a) *Benzylamine.* A solution of 3.0 ml. (0.043 mole) of iodine pentafluoride in 120 ml. of methylene chloride was cooled to 3° and 4.3 g. (0.040 mole) of benzylamine in 30 ml. of methylene chloride was added dropwise over 30 min. The solution was stirred at 15° for 2 hr. Ice water then was added and the methylene chloride was separated and washed with dilute hydrochloric acid, water, and dilute sodium thiosulfate solution. Evaporation of the methylene chloride left 1.35 g. of residue. The infrared spectrum of this oil indicated that it was a benzonitrile-benzaldehyde mixture. The sample was chromatographed on Perkin-Elmer vapor phase chromatogram Column A at 150°, utilizing acetophenone as an internal standard. In this way it was determined that the residue consisted of benzaldehyde, 0.84 g. (20%), and benzonitrile, 0.35 g. (9%). The retention time of the benzaldehyde and of the benzonitrile was the same as that of the authentic material used in obtaining the calibration curves.

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[2] M. C. Sneed, J. L. Maynard, and R. C. Brasted, *Comprehensive Inorganic Chemistry*, Vol. III, *The Halogens*, D. Van Nostrand Co., Inc., New York, N. Y., 1954, pp. 210–13; General Chemical Division, Allied Chemical and Dye Corporation, Technical Bulletin TA-8532-2, "Chlorine Trifluoride and Other Halogen Fluorides."

[3] As a referee has pointed out, there is an analogy between these dehydrogenations and those reported in the Hofmann rearrangement for certain amines of intermediate size [see E. S. Wallis and J. F. Lane, *Org. Reactions*, **3**, 267 (1946)]. One could postulate the formation of *N*-fluoroamine intermediates in these oxidations, as *N*-bromoamines were considered to be intermediates in the hypobromite oxidations (R. C. Fuson, *Advanced Organic Chemistry*, John Wiley and Sons, New York, 1950, p. 538), but no evidence was found for such species. The basic fractions of these reactions, and of those mentioned later, were not examined for coupling products.

[4] E. Farenhorst and E. C. Kooyman, *Rec. trav. chim.*, **72**, 993 (1953).

TABLE I

Iodine Pentafluoride Reactions

Organic Compound	Solvent[a]	Substrate, mmoles	IF_5, mmoles	Reaction Conditions	Products, mmoles
Benzylamine	C	40	43	15°, 2 hr.	Benzaldehyde, 8[b] Benzonitrile, 4[b]
Benzylamine	CP	40	43	15°, 2 hr.	Benzonitrile, 36[b] Benzaldehyde, Trace
Hexylamine	CP	70	71	25°, 4 hr.	Hexanenitrile, 36
Butylamine	CP	40	43	20°, 2 hr.	Butyronitrile, 17
Isobutylamine	CP	40	43	20°, 2 hr.	Isobutyronitrile, 14[b] Isobutyraldehyde, 10[b]
t-Butylamine	CP	100	70	−10°, 1 hr. 3°, 1 hr.	Azoisobutane, 24 (48%)
Hydrazobenzene	C	29	14	3°, 1 hr.	Azobenzene, 10.5 (74%)
Dibenzylamine	CP	20	43	15°, 2 hr.	Benzaldehyde, 16
Tribenzylamine	C	20	43	15°, 2 hr.	Benzaldehyde, 18 Dibenzylamine, 12
Cyclohexanone oxime	C	43	43	3°, 1 hr. 15°, 1 hr.	ε-Caprolactam, 12.5
Benzophenone oxime	C	43	43	3°, 1 hr. 15°, 1 hr.	*N*-Phenylbenzamide, 32
Acetophenone oxime	C	43	43	3°, 1 hr. 15°, 1 hr.	Acetophenone, 9 Acetanilide, 9.3 *p*-Iodoacetanilide, 2.3

[a] Solvent C is methylene chloride; CP is a methylene chloride–pyridine mixture. [b] Yield determined by vapor phase chromatography.

A 0.26-g. portion of the reaction product was added to a solution of 2,4-dinitrophenylhydrazine; a total of 0.45 g. (67%) of the 2,4-dinitrophenylhydrazone of benzaldehyde was collected, m.p. and mixture m.p. 235–236°.

When the reaction was conducted as described above, except that 13 ml. (0.16 mole) of pyridine was added to the solution, there was obtained 3.86 g. of residue. This residue was analyzed by vapor phase chromatography and was found to contain benzonitrile, 3.68 g. (89%), and a little benzaldehyde (about 3%).

(b) *Hexylamine.* A solution containing 5.0 ml. (0.071 mole) of iodine pentafluoride, 23 ml. (0.28 mole) of pyridine, and 150 ml. of methylene chloride was stirred at 3° while 9.3 ml. (0.070 mole) of hexylamine in 20 ml. of methylene chloride was added dropwise. The mixture was stirred at 25° for 4 hr, then water was added and the organic layer was separated. The methylene chloride solution was washed successively with water, dilute hydrochloric acid, water, 5% aqueous sodium thiosulfate, and water. The methylene chloride was removed by distillation and the residue was distilled to give hexanenitrile, 3.67 g. (52%), b.p. 72° (33 mm.), n_D^{20} 1.4069. The nitrile sample gave only a single peak on examination by vapor phase chromatography; the retention time was the same as that of the authentic sample. However, the authentic sample contained a second small peak that was not removed by distillation, and the lack of a pure reference sample prevented a v.p.c. yield from being determined.

(c) *Hydrazobenzene.* A solution of 5.35 g. of hydrazobenzene in 40 ml. of methylene chloride was added to a stirred solution of 1.0 ml. (0.014 mole) of iodine pentafluoride in 50 ml. of methylene chloride. A cooling bath maintained an internal temperature of −10° to −5° during the addition; the mixture then was stirred 1 hr. at 3°. The reaction mixture was quenched in water, and the organic layer was processed as usual. The residue obtained on evaporation of the methylene chloride was chromatographed on silica gel. Azobenzene, 3.84 g. (74%), m.p. 66–67°, was obtained on evaporation of the pentane–methylene chloride eluate. The product was identified by mixture melting point and infrared spectrum.

(d) *t-Butylamine.* A solution containing 120 ml. of methylene chloride, 18 ml. of pyridine, and 5.0 ml. (0.07 mole) of iodine pentafluoride was stirred at −10° while 7.3 g. (0.10 mole) of *t*-butylamine in 10 ml. of methylene chloride was added dropwise. The mixture then was stirred at −10° for 1 hr. and at 0° for 1 hr. Water was added and the organic layer was separated and washed with water, dilute hydrochloric acid, 5% aqueous sodium thiosulfate, and water. The methylene chloride was removed through a Holzman column and the residue was distilled through the same column. 2,2′-Dimethyl-2,2′-azopropane, 3.40 g., b.p. 53° (70 mm.), n_D^{20} 1.4133, reported[4] b.p. 109° (45°/50 mm.), n_D^{20} 1.4091. The vapor phase chromatogram of the material on Perkin Elmer Column A at 75° exhibited 2 trace impurities. A redistilled center cut had n_D^{20} 1.4193; the trace impurity peaks were still present in the vapor phase chromatogram.

Anal. Calcd. for $C_8H_{18}N_2$: C, 67.55; H, 12.75; N, 19.70. Found: C, 67.83; 11.71; N, 19.72.

Reaction of acetophenone oxime and iodine pentafluoride. A stirred solution of 3.0 ml. (0.043 mole) of iodine pentafluoride in 120 ml. of methylene chloride was cooled in an ice bath while 5.8 g. (0.043 mole) of acetophenone oxime in 30 ml. of methylene chloride was added dropwise. Stirring was continued for 1 hr. at 3° and for 1 hr. at 15°. Water was then added and the organic layer was separated and washed with 15% aqueous sodium thiosulfate and water. The residue obtained on evaporation of the methylene chloride was chromatographed on silica gel. The first fraction eluted from the column was acetophenone, 1.09 g. (21%), identified as its 2,4-dinitrophenylhydrazone, m.p. 235–237°, mixture m.p. 236–237° (authentic sample m.p. 242–243°); the infrared spectrum of the derivative was identical with that of acetophenone 2,4-dinitrophenylhydrazone. A second fraction (3.33 g.) was eluted by methylene chloride–methanol. This was recrystallized from ethanol-water to give (a), 0.83 g., m.p. 162–166°, (b) 0.83 g., m.p. 108–111°, (c) 0.46 g., m.p. 113–114°, and (d) 0.14 g., m.p. 113–114°. The last 2 fractions were acetanilide; a mixture m.p. with acetanilide was 113–114°. The (a) and (b) crops were recrystallized from ethanol to give *p*-iodoacetanilide, 0.55 g., m.p. 180–182°; a mixture m.p. with an authentic sample (m.p. 184–186°) was 182–184°. A second crop of less pure *p*-iodoacetanilide, 0.06 g., m.p. 168–172 was also obtained. A final crop of acetanilide, 0.67 g., 109–111°, mixture m.p. 112–113°

was obtained from the mother liquors of the (a) and (b) recrystallization.

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Evidence for the Expansion of the Valence Shell of Divalent Sulfur[1]

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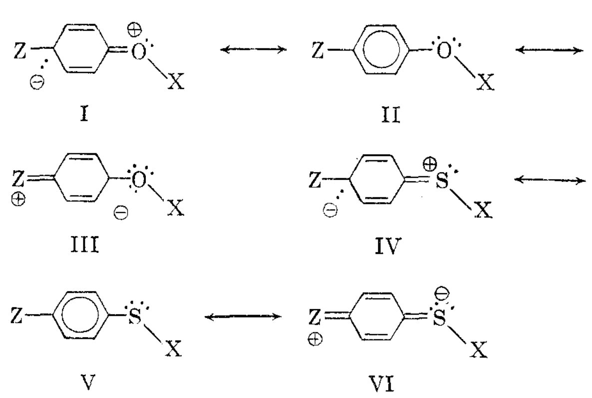
Because sulfur has unoccupied 3*d*-orbitals, it has the possibility of expanding its valence shell through electron-pair acceptor type conjugation. When sulfur is attached directly to a phenyl ring this electron-pair acceptor conjugation presumably occurs *via* overlap between a π-orbital on carbon and an unoccupied 3*d*-orbital on sulfur to form a $(p\text{-}d)\pi$ bond.

Bordwell and Boutan[2] concluded on the basis of pK_a data and a qualitative Hammett σ treatment that electron-pair acceptor type conjugation for divalent sulfur is usually small or negligible. Application of recent modifications of the Hammett σ treatment[3] which allow semiquantitative evaluation of resonance effects demonstrates that some revision of these conclusions is necessary.

Bordwell and Boutan reasoned that if sulfur expanded its valence shell the resonance form (VI) would be more important than form (III) and a $-$R *para*- substituent (Z) would be more electron donating by resonance in the ionization of a substituted thiophenol than in the ionization of the corresponding phenol, *i.e.*, the resonance effect of a $-$R *para*- substituent (Z) would have a larger negative value in the ionization of a thiophenol than in that of the corresponding phenol.[4]



They looked for this resonance effect, but their treatment of the data did not show it (*cf.* results listed in Table I) and it was therefore assumed to be absent. However, they arrived at their conclusions *via* the qualitative relationship:

$$\sigma_p - \sigma_m \cong para\text{-resonance effect}$$

which neglects small but significant resonance effects due to *meta*- substituents. Resonance values ($\bar{\sigma}_R$) calculated by the method of Taft and Lewis[3] (given in Table I), which considers resonance interactions from the *meta*- position, show that the effect is present, and although small, is outside of experimental error.

TABLE I

COMPARISON OF ($\sigma_p - \sigma_m$) VALUES WITH $\bar{\sigma}_R$VALUES

Z	$\sigma_p - \sigma_m$ (ionization of phenols)	$\sigma_p - \sigma_m$ (ionization of thiophenols)	$\bar{\sigma}_R$[a] (ionization of phenols)	$\bar{\sigma}_R$[a] (ionization of thiophenols)
$-OCH_3$	-0.24	-0.21	-0.36	-0.48
$-N(CH_3)_2$	-0.16	-0.17	-0.21	-0.33

[a] These $\bar{\sigma}_R$ values were calculated using the ρ_I values given in Table II of reference (3) and the aliphatic σ_I values given by Taft and Lewis in Table I of reference (3) and Table II of *J. Am. Chem. Soc.*, **80**, 2436 (1958).

Participation by sulfur in electron-pair acceptor type conjugation should increase as the X-group attached to sulfur becomes more electron withdrawing by inductive and conjugative interaction (as measured *qualitatively* by the σ_p value of the X-group). This follows since such withdrawal would reduce the contribution of resonance form (IV) and also contract the 3*d*-orbitals making them less diffuse and therefore capable of greater overlap with a 2*p*-orbital on carbon. Table II shows that this effect is actually observed. The $\bar{\sigma}_R$ values for $-\ddot{\mathrm{S}}\diagdown_{\mathrm{X}}$ qualitatively follow the σ_p values of X, increasing from negative numbers (net electron doner action by $-\ddot{\mathrm{S}}\diagdown_{\mathrm{X}}$) when X is CH_3 to *positive* numbers (net electron acceptor action by $-\ddot{\mathrm{S}}\diagdown_{\mathrm{X}}$) when X is $COCH_3$ and CN. In each case the $\bar{\sigma}_R$ values are *more positive* for the ionization of the substituted phenol than for that of the corresponding substituted benzoic acid, as would be expected

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(2) F. G. Bordwell and P. J. Boutan, *J. Am. Chem. Soc.*, **78**, 854 (1956).

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

(4) As a result of resonance form (VI), valence shell expansion by sulfur would be expected to stabilize the substituted thiophenol relative to the corresponding thiophenylate ion because of the negative charge on sulfur in the anion. This effect should be very much smaller in the case of the substituted phenols; consequently, the ionization constant of thiophenol would be decreased more by the introduction of a $-$R *para* substituent (Z) than would the ionization constant of phenol.