Under similar conditions *p*-iodoaniline yielded a quantitative amount of aniline hydroiodide in 1 hr, *o*-bromoaniline produced a 78.4% yield of aniline hydrobromide in 6 hr, and *p*-chloroaniline produced a 15.8% yield of aniline hydrochloride in 96 hr. Neither *p*-fluoro- nor *m*-bromoaniline showed evidence of hydrogenolysis with thiophenol.

Hydrogenolysis of *p*-Iodonitrobenzene.—A mixture of 6.1 g (0.024 mol) of *p*-iodonitrobenzene, 10 ml of thiophenol, and 10 ml of aniline was heated to reflux for 17 hr. Aniline hydriodide (2.4 g, 44.3%) was isolated from the reaction mixture by aqueous extraction. Under similar conditions, *p*-bromonitrobenzene gave no evidence for hydrogenolysis.

A similar reaction without ainiline was studied to see if nitrobenzene could be isolated from the hydrogenolysis of *p*-iodonitrobenzene. A solution of 10 g (0.04 mol) of *p*-iodonitrobenzene and 60 ml of thiophenol was refluxed for 7 hr. The precipitate formed was collected, washed with ether, and dissolved in water. The solution was made alkaline with NaOH and extracted with ether. Removal of the solvent left 1 g (27% yield) of aniline identified by retention time on a 6-ft 3% SE-30 column at 100° in a Hewlett-Packard Model 402 gas chromatograph. Apparently an oxidation–reduction reaction occurs between thiophenol and the nitro group. No nitrobenzene was observed in the gc. Treatment of nitrobenzene with thiophenol under similar conditions gave little aniline; thus the reduction observed must be intimately associated with the hydrogenolysis reaction.

Hydrogenolysis of Iodobenzene.—A solution of 10.0 g (0.05 mol) of iodobenzene, 10 ml of thiophenol, and 10 ml of aniline was heated to reflux for 7 days. Aniline hydriodide (1.0 g, 9.0% yield) was isolated from the reaction mixture by collection of the solid. From a similar reaction, a gc of the filtrate on a 6-ft 3% SE-30 column at 65° in a Hewlett-Packard Model 402 gas chromatograph showed the presence of a small amount of benzene identified by retention time of an authentic sample.

Attempted Radical Initiation.—No reaction between thiophenol and *p*-bromoaniline was observed at 100° with or without the addition of AIBN.

Registry No.—Thiophenol, 108-98-5; *p*-bromoaniline, 106-40-1; *p*-iodoaniline, 540-37-4; *o*-bromoaniline, 615-36-1; *p*-chloroaniline, 106-47-8; *p*-iodonitrobenzene 636-98-6; iodobenzene, 591-50-4.

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The Addition of *tert*-Butyl Hypochlorite to Isocyanates[1]

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Addition of *tert*-butyl hypochlorite (**2**) to an isocyanate (**1**) gives an unisolated *N*-chlorocarbamate (**3**). Previously known adducts required insertion of the azomethine linkage of an isocyanate into the single bond between (1) hydrogen and each of many elements; (2) oxygen and certain elements, *e.g.*, titanium, tin, and carbon (the reactive ether linkage in orthoformates, formaldehyde acetals, and epoxides); (3) silicon and nitrogen; (4) boron and sulfur; and (5) phosphorus and chlorine.[2] The present work is terminal and grew out of a continuing study of the relationship between an *N*-acylimine and the isomeric isocyanate, $R_2C{=}NC({=}O)Z$ and $R_2C(Z)N{=}C{=}O$.

Under mild conditions the hypochlorite **2** combined with cyclohexyl, benzhydryl, and phenyl isocyanates (**1a–c**). An assumed initial formation of an undetected *N*-chlorocarbamate (**3**) provided an explanation for each product formation. From **3a** hydrolysis during work-up produced *N*-cyclohexylcarbamate (**4a**) and dehydrochlorination to a small extent gave the *N*-*tert*-butoxycarbonylimine (**5a**) of cyclohexanone, detected by hydrolysis into *tert*-butyl carbamate and a product (**6**) in low yield which appears to be a hydrogen chloride adduct.[3]

At 70° an adduct obtained from the neat mixture of **2** and benzhydryl isocyanate (**1b**) underwent dehydrochlorination, affording the *N*-*tert*-butoxycarbonylimine (**5b**) of benzophenone in 87% yield. Identification of benzophenone and *tert*-butyl carbamate, obtained upon hydrolysis, confirmed the structure of the imine. In contrast with the thermolysis of the *N*-benzoylimine of benzophenone at 110–115° into benzophenone[4] (and presumably benzonitrile) the ester **5b** was thermally stable under 170°. At 180° it fragmented to give the imine of benzophenone in 57% yield, but the ketone itself was not detected. Presumably carbon dioxide and isobutylene were also formed.

An apparent rearrangement of the *N*-chloro-*N*-phenylcarbamate (**3c**), obtained from **2** and **1c**, gave both *o*- and *p*-chlorophenylcarbamates (**7** and **8**), with the latter in slight predominance.[5] Each was identified by saponification and decarboxylation into the corresponding chloroaniline.

$$\underset{\mathbf{1}}{RNCO} + \underset{\mathbf{2}}{(CH_3)_3COCl} \longrightarrow \underset{\mathbf{3}}{RN(Cl)CO_2C(CH_3)_3}$$

$$\mathbf{a},\ R = \overparen{\underparen{(CH_2)_5CH}};\ \mathbf{b},\ R = (C_6H_5)_2CH;\ \mathbf{c},\ R = C_6H_5$$

$$\underset{\mathbf{4}}{R'_2CHNHCO_2C(CH_3)_3} \xleftarrow{H_2O} \underset{\mathbf{3}}{R'_2CHN(Cl)CO_2C(CH_3)_3} \xrightarrow{-HCl} \underset{\mathbf{5}}{R'_2C{=}NCO_2C(CH_3)_3}$$

$$\mathbf{a},\ R'_2 = (\overset{|}{\underset{|}{C}}H_2)_5;\ \mathbf{b},\ R' = C_6H_5$$

$$\mathbf{5a} \xrightarrow{HCl} \underset{\mathbf{6}}{R_2'C(Cl)NHCO_2C(CH_3)_3}$$

$$\mathbf{3c} \longrightarrow o\text{-}\mathbf{7} \text{ and } \underset{\mathbf{8}}{p\text{-}ClC_6H_4NHCO_2C(CH_3)_3}$$

$$\mathbf{5b} \xrightarrow{180^\circ} (C_6H_5)_2C{=}NH + [(CH_3)_2C{=}CH_2 + CO_2]$$

Experimental Section

***tert*-Butyl *N*-Cyclohexylcarbamate (4a).**—A mixture of 5.5 g (44.0 mmol) of cyclohexylisocyanate and 5.1 g (47.0 mmol) of *tert*-butyl hypochlorite in 30 ml of petroleum ether (bp 30–60°) was stirred at room temperature for 15 hr in a 50-ml three-necked round-bottom flask equipped with a stream of dry nitrogen, a stirrer, and a condenser with a drying tube. Unreacted isocyanate, detected by ir absorption at 2250 cm^{-1}, disappeared

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[1] Financial support was received from NASA Grant No. NGR 14-012-004.

[2] S. Ozaki, private communication.

[3] A referee suggests an alternative transformation which does not require the assumption that water is available during chromatography: $\mathbf{3} + HCl\ (anhydrous) \rightarrow \mathbf{4} + Cl_2$.

[4] R. Ahmed and W. Lwowski, *Tetrahedron Lett.*, 3611 (1969).

[5] Migration of chlorine in *N*-chloroacetanilide gives *o*- (32.5%) and *p*-chloroacetanilide (67.5%) as reported by J. Kennedy, P. Orton and A. E. Bradfield, *J. Chem. Soc.*, 986 (1927). The evidence indicates an intermolecular process: J. March, "Advanced Organic Chemistry: Reactions, Mechanisms, and Structure," McGraw-Hill, New York, N. Y., 1968, p 431.

after 15 ml of absolute ethanol was added with thorough stirring. Solvents were removed and the residue was separated from a column of silica gel (15 × 0.5 in.). The carbamate **4a** was eluted with 900 ml of a 1:1 mixture of *n*-hexane and benzene; after removal of solvent, sublimation at 40° (0.4 mm) gave 3.16 g (39.2%) of a colorless powder, mp 78–79.5° dec, identical by melting point and ir comparison with an authentic sample prepared from cyclohexyl isocyanate and *tert*-butyl alcohol, ir ($CHCl_3$) 3470 (NH), 1705 (CO), and 1510 cm^{-1} (secondary amide). Next the chlorocyclohexylcarbamate **6** was eluted with 300 ml of a 1:2 mixture of *n*-hexane and benzene; after removal of solvent, sublimation at 80° (0.4 mm) gave 112 mg (1.2%) of a colorless powder: mp 124–125.5°; ir ($CHCl_3$) 3450 (NH), 1705 (CO), and 1495 cm^{-1} (secondary amide). *Anal.* Calcd for $C_{11}H_{20}NO_2Cl$: C, 56.52; H, 8.62; N, 5.99; Cl, 15.16. Found: C, 56.31; H, 8.71; N, 5.82; Cl, 15.47.

A third component was eluted with 300 ml of chloroform; after removal of solvent, sublimation at 40° (0.4 mm) gave 0.11 g (2.1%) of *tert*-butyl carbamate as colorless needles, mp 106–108°. Finally 600 ml of 95% ethanol removed cyclohexylamine hydrochloride; after removal of solvent, sublimation at 120° (0.4 mm) gave 1.26 g (21.1%) of a colorless powder, mp 204° dec. Both *tert*-butyl carbamate and cyclohexylamine hydrochloride were identical with authentic samples.

In a similar reaction between benzhydryl isocyanate and *tert*-butyl hypochlorite (in a molar excess) without a solvent at 70°, the ester **5b** was isolated by sublimation at 85° (0.4 mm) in 87% yield: ir ($CHCl_3$) 1725 (CO) and 1625 cm^{-1} (C=N); nmr ($CDCl_3$) δ 7.5 (s, 10, C_6H_5), 1.3 [s, 9, $(CH_3)_3C$]; mass spectrum (70 eV) *m/e* 281 (M^+). *Anal.* Calcd for $C_{18}H_{19}NO_2$: C, 76.84; H, 6.81; N, 4.97; mol wt, 281.36. Found: C, 76.58; H, 6.83; N, 4.94. Hydrolysis gave *tert*-butyl carbamate and benzophenone, identified by comparison with authentic data. Decomposition resulted from heating in a sealed melting point tube at 180° for 2 hr. Dissolving the combined residues from six tubes containing a total of 56 mg of **5b** in petroleum ether which was then saturated with a stream of anhydrous hydrogen chloride gave 25 mg (57%) of the hydrochloride of the imine of benzophenone, sublimation point 250°,[6] ir absorption identical with an authentic spectrum.

From phenyl isocyanate and *tert*-butyl hypochlorite in equimolar portions in petroleum ether at room temperature *o*- (**7**) and *p*-chlorophenylcarbamate (**8**) were obtained by elution from silica gel with hexane. The ortho isomer separated first, 1.7 g (17.7%) after distillation at 120–122° (0.4 mm). Redistillation gave a yellow liquid with constant $n^{25}D$ 1.5231; ir ($CHCl_3$) 3420, 1725, and 1510 cm^{-1}; nmr ($CDCl_3$) δ 8.37–8.22 (br, 1, NH), 7.32 (m, 4, C_6H_4), 1.52 [s, 9, $(CH_3)_3C$]; mass spectrum (70 eV) *m/e* 227 (M^+). *Anal.* Calcd for $C_{11}H_{14}NO_2Cl$: C, 58.02; H, 6.19; N, 6.15; Cl, 15.57; mol wt, 227.69. Found: C, 57.82; H, 6.16; N, 6.12; Cl, 15.55.

The para isomer **8** sublimed at 80° (0.4 mm) and gave 2.27 g (23.5%) of a colorless powder, mp 95–99°, which recrystallized from *n*-heptane as needles: mp 102–104°; ir ($CHCl_3$) 3420, 1725, and 1510 cm^{-1}; nmr ($CDCl_3$) δ 7.28 (m, 4, C_6H_4), 6.7 (br, 1, NH), 1.5 (s, 9, $(CH_3)_3C$]; mass spectrum (70 eV) *m/e* 227 (M^+). Chloroform eluted *N,N'*-diphenylurea identified by comparison with authentic data.

Registry No.—**2**, 507-40-4; **4a**, 3712-40-1; **5b**, 35426-67-6; **6**, 35426-68-7; **7**, 35426-69-8; **8**, 18437-66-6.

(6) R. Appel and A. Hauss, *Chem. Ber.*, **93**, 405 (1960).

Anomalous Properties of Halogen Substituents

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The electron-attracting tendencies of halogen substituents in aliphatic compounds are well established, on the basis of such familiar evidence as the increase in the acidity of carboxylic acids[1] and many other organic compounds[2,3] upon substitution by halogens. A quantitative measure of this "inductive effect" is the substituent constant σ_I.[4,5] The values of σ_I for the halogens are given in Table I; as anticipated, they show the same trend as the electronegativities of these elements.

Table I

Halogen Electronegativities and Substituent Constants

Halogen	Electronegativity[a]	σ_I[b,c]	σ_R[b,c]
F	4.0	+0.51	−0.34
Cl	3.0	+0.47	−0.20
Br	2.8	+0.45	−0.16
I	2.5	+0.39	−0.12

[a] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960. [b] P. R. Wells, S. Ehrenson, and R. W. Taft, in "Progress in Physical Organic Chemistry," Vol. 6, A. Streitwieser and R. W. Taft, Ed., Interscience, New York, N. Y., 1968. [c] The more positive the value of σ_I, the greater is the electron-attracting tendency; the more negative the value of σ_R, the greater is the electron-donating tendency.

These electron-attracting powers are presumably also operative when the halogens are substituents on aromatic rings; indeed, the halobenzenes are less reactive toward electrophilic attack than is benzene.[6] However, substituents which simply withdraw electrons from the ring are found to be meta directing,[7] whereas the halogens are ortho and para directing.[6,7] This is generally interpreted as indicating a concomitant donation, or feedback, of electrons to the ring by the halogen substituent,[7,8] and is usually described as a "resonance effect." Surprisingly, this supposed electron-donating tendency increases in the order I < Br < Cl < F; the greatest feedback seems to occur when the substituent is fluorine, the most electronegative element. For instance, fluorine deactivates a benzene ring less than does chlorine,[6] and in fact, using partial rate factors, some electrophilic substitutions are found to occur more rapidly at the para position in fluorobenzene than at any single position in benzene. Relatively stable protonated fluorobenzenes have even been observed.[9] The extent of this "resonance effect" is measured by another substituent constant, σ_R (Table I).[10]

The trend in the supposed electron-donating powers, as indicated by the σ_R values, and especially the be-

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(1) See, for example, R. T. Morrison and R. N. Boyd, "Organic Chemistry," 2nd ed, Allyn and Bacon, Boston, Mass., 1966.

(2) J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1962.

(3) B. L. Dyatkin, E. P. Mochalina, and I. L. Knunyants, *Tetrahedron*, **21**, 2991 (1965).

(4) R. W. Taft in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956.

(5) R. W. Taft, *J. Phys. Chem.*, **64**, 1805 (1960); R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Anderson, and G. T. Davis, *J. Amer. Chem. Soc.*, **85**, 709 (1963).

(6) L. M. Stock and H. C. Brown in "Advances in Physical Organic Chemistry," Vol. 1, V. Gold, Ed., Academic Press, New York, N. Y., 1963.

(7) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969.

(8) W. A. Sheppard and C. M. Sharts, "Organic Fluorine Chemistry," W. A. Benjamin, New York, N. Y., 1969. This book gives an excellent review of many of the points discussed in this paper.

(9) G. A. Olah and T. E. Kiovsky, *J. Amer. Chem. Soc.*, **89**, 5692 (1967).

(10) R. W. Taft and I. C. Lewis, *ibid.*, **81**, 5343 (1959); R. W. Taft, E. Price, I. R. Fox, I. C. Lewis, K. K. Andersen, and G. T. Davis, *ibid.*, **85**, 3146 (1963).