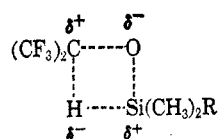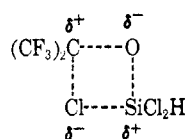formation of a hexafluoroisopropoxide anion $HC(CF_3)_2$-O^-. However, the formation of a discrete anion, accompanied by the corresponding siliconium ion, is unnecessary. The results are explained equally well by a four-center transition state of the type

$$
\begin{array}{cc}
\delta^+ & \delta^- \\
(CF_3)_2\overset{|}{C}\text{-----}\overset{|}{O} \\
\overset{|}{H}\text{-----}\overset{|}{Si}(CH_3)_2R \\
\delta^- & \delta^+
\end{array}
$$

followed by formation of the C–H and Si–O bonds to give 1 and 2. The present work with hexafluoroacetone and trichlorosilane tends to support this idea since the production of 6 and 7 can be explained by an analogous electrophilic attack of the carbonyl carbon on the chlorine atom of the silicon–chlorine bond, with formation of a four-center transition state similar to that already described.

$$
\begin{array}{cc}
\delta^+ & \delta^- \\
(CF_3)_2\overset{|}{C}\text{-----}\overset{|}{O} \\
\overset{|}{Cl}\text{-----}\overset{|}{Si}Cl_2H \\
\delta^- & \delta^+
\end{array}
$$

Any discrete anion formed would necessarily be the 2-chlorohexafluoroisopropoxide ion, a species which Janzen and Willis[8] have rejected as being unlikely owing to the poor nucleophilicity of the chloride ion. A similar mechanism has been proposed for the reaction of hexafluoroacetone with alkoxysilanes.[9] The small amount of dialkoxysilane 7 produced in the reaction results simply by the combination of 6 with another mole of ketone, by the pathway already outlined.

It thus appears that reactions between perhalo ketones and silanes may proceed by two distinct pathways, depending on the reaction conditions employed. In the liquid phase, in the absence of any radical initiator, the four-center mechanism as outlined above accounts for the products observed. Our results with hexafluoroacetone and trichlorosilane corroborate this suggestion. In the presence of ultraviolet light, a free-radical chain reaction mechanism seems most probable.[10] In the case of the nonhalogenated silanes used in the experiments, both pathways lead to the same product, and no attempt has been made to distinguish between the two, although it is doubtful that a radical mechanism could be operative under the conditions employed here. Only in the case of a suitably substituted silane, such as trichlorosilane, are the two mechanisms readily resolved.

Experimental Section

Volatile materials were manipulated in a vacuum manifold system. The perhalo ketones are products of Allied Chemical Corp. and were used without further purification. All silanes were purchased from Peninsular ChemResearch, Inc. Elemental analyses were carried out by Schwarzkopf Microanalytical Laboratory, and nuclear magnetic resonance spectra were obtained on a Varian A-60 instrument at 60 MHz. Spectral data for new compounds are summarized in Table II.

In general, the reactions were carried out in glass Fisher-Porter Aerosol compatibility tubes, although some large-scale runs were made in a 300-ml stainless steel pressure reactor. Re-

(9) R. A. Braun, *Inorg. Chem.*, **5**, 1831 (1966).
(10) C. G. Krespan and W. J. Middleton, *Fluorine Chem. Rev.*, **1**, 145 (1967).

actions were continued until the rate of pressure decrease was minimal. The reaction between hexafluoroacetone and trichlorosilane is given below as a typical experimental procedure.

Reaction of $(CF_3)_2CO$ and Cl_3SiH.—Trichlorosilane (16 g, 0.118 mol) was placed in a glass compatibility tube, which was then cooled to $-78°$. The free space over the silane was evacuated, and hexafluoroacetone (23.5 g, 0.141 mol) was introduced through a vacuum manifold system. The glass tube contained a small, plastic-covered magnetic stirring bar, and the liquid contents of the tube were stirred overnight at ambient temperature. No reaction was apparent so the tube was warmed to 45°. The autogenous pressure rose to 75 psig and gradually fell, over a 70-hr period, to 20 psig. Distillation of the contents of the tube gave 4.1 g of unreacted Cl_3SiH; 13.3 g of $ClC(CF_3)_2$-$OSiCl_2H$, bp 86°; and 5.2 g of $[Cl(CF_3)_2O]_2SiClH$, bp 136°.

Substituent Effects and Thermodynamic Consequences of Linear Free-Energy Relations

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There is now considerable empirical support for various linear free-energy relations as accurate and economical correlations of effects of substituents on organic molecules. Possibly the best known and most widely used linear free-energy relation is the Hammett equation that is written as in eq 1. Since we are

$$\log K = \rho\sigma \tag{1}$$

specifically concerned with application of this equation to acid–base equilibria in solution, K represents equilibrium constants for reactions of the type given in

$$HA(S) + R^-(S) = A^-(S) + HR(S) \tag{2}$$
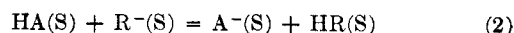
where HR represents the parent or reference acid and HA represents the substituted acid of interest. The symbol (S) is used to denote that the preceding species is in solution. The constant σ is intended to depend only on the substituent, but ρ depends on the particular reaction under consideration and also on both the solvent and the temperature.

Since the empirical successes of the Hammett equation are well known, we turn to careful consideration of some of its thermodynamic implications. Taking the substituent constant σ to be independent of temperature, we differentiate eq 1 with respect to temperature to obtain eq 3 and 4. These equations

$$\Delta H° = [2.3RT^2(\partial\rho/\partial T)]\sigma = -(\partial \ln \rho/\partial \ln T)\Delta G° \tag{3}$$

$$\Delta S° = 2.3R[\rho + T(\partial\rho/\partial T)]\sigma = \\ -[(1/T) + (\partial \ln \rho/\partial T)]\Delta G° \tag{4}$$

indicate that $\Delta H°$ and $\Delta S°$ values for reactions of the type in eq 2 should be proportional to σ and $\Delta G°$

values. Further differentiation of eq 3 or 4 leads to $\Delta C_p{}^\circ$ proportional to ΔS°.

As pointed out previously,[2] it is convenient to work out a thermodynamic theory of reactions of type 2 in terms of ΔH° and ΔS° values for such reactions. To indicate specifically that these ΔH° and ΔS° values are considered as sums of external (environmental) and internal contributions as previously defined,[2,3] we write eq 5 and 6.

$$\Delta H^\circ = \Delta H_{int} + \Delta H_{ext} \qquad (5)$$

$$\Delta S^\circ = \Delta S_{int} + \Delta S_{ext} \qquad (6)$$

Earlier investigations[2] have shown that $\Delta S^\circ{}_{int} \cong 0$ for most reactions of type 2 and suggest that ΔH_{ext} is proportional to ΔS_{ext} or ΔS° as indicated by eq 7.

$$\Delta H_{ext} = \beta \Delta S^\circ \qquad (7)$$

Combination of these relations with $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$ leads to

$$\Delta G^\circ = \Delta H_{int} + (\beta - T)\Delta S^\circ \qquad (8)$$

Since considerable evidence[2-9] indicates that $\beta \cong T$, we obtain eq 9 and 10 in which we identify $C/2.3RT$

$$\Delta G^\circ \cong \Delta H_{int} \qquad (9)$$

$$\rho\sigma = -\Delta H_{int}/2.3RT = (C/2.3RT)(-\Delta H_{int}/C) \qquad (10)$$

with ρ and $-\Delta H_{int}/C$ with σ in the Hammett equation (eq 1). Many data[9-11] confirm that ρ varies linearly with $1/T$, and it has also been found that ΔH_{int} values calculated from $\Delta H_{int} = \Delta H^\circ - \beta\Delta S^\circ$ are indeed proportional to appropriate σ (and σ^*) values. It should come as no surprise that σ and σ^* values are proportional to ΔH_{int} values, since the tabulated σ and σ^* values are based on ΔG° values and we have $\Delta G^\circ \cong \Delta H_{int}$ in eq 9.

Differentiation of eq 9 written as an equality with ΔH_{int} taken to be independent of temperature leads to $\Delta S^\circ = 0$, which is known to be untrue in many instances, and is not in agreement with ΔS° proportional to σ or ΔG° as derived from the Hammett equation as in eq 4. This treatment (eq 5–10) is useful in that it shows how compensation of ΔH_{ext} and $T\Delta S_{ext}$ (with $\beta \cong T$) leads to $\Delta G_{ext} \cong 0$ and thence to the useful approximation (eq 9).

If we have (nearly) complete compensation of ΔH_{ext} by $T\Delta S_{ext}$ so that $\Delta G_{ext} \cong 0$, it then follows that $\Delta G^\circ \cong \Delta H_{int}$ and we have a linear free-energy equation of the familiar form. This sort of compensation gives ΔG° for reactions of type 2 independent of the solvent, which means that the Hammett ρ should be independent of the solvent. But Wells[11] has shown that ρ values *do* depend on the solvent. A theoretical solution to this difficulty involves introduction of new information (or parameters) while maintaining already satisfactory features of previous treatments that lead

to some understanding of compensation and linear free-energy relations.

The incomplete compensation of ΔH_{ext} by $T\Delta S_{ext}$ must ultimately be described in terms of details of interactions between the solute species and the solvent, which in turn involves the details of the structures of the molecules. Since ΔH_{int} values are also related to these latter properties of the solute species, we suggest that incomplete compensation is approximated by

$$\Delta H_{ext} - \beta\Delta S^\circ = \gamma\Delta H_{int} \qquad (11)$$

In eq 11 and subsequent equations, γ is a parameter that depends on the solvent and relates the details of solute–solvent interactions to the incompleteness of compensation. As will be shown, introduction of the single parameter γ remedies several difficulties in earlier treatments.

We now proceed as before to obtain

$$\Delta H^\circ = \Delta H_{int}(1 + \gamma) + \beta\Delta S^\circ \qquad (12)$$

and

$$\Delta G^\circ = \Delta H_{int}(1 + \gamma) + (\beta - T)\Delta S^\circ \qquad (13)$$

Since the present extended treatment requires no change in the previously cited conclusions that $\beta \cong T$, we simplify eq 13 to obtain eq 14. Combination of

$$\Delta G^\circ \cong \Delta H_{int}(1 + \gamma) \qquad (14)$$

eq 14 with the Hammett equation leads to

$$\rho\sigma = [C(1 + \gamma)/2.3RT](-\Delta H_{int}/C) \qquad (15)$$

in which we identify ρ with $C(1 + \gamma)/2.3RT$ and σ with $-\Delta H_{int}/C$. Thus eq 15 properly predicts the temperature dependence of ρ *and* allows ρ to depend on the solvent.

Differentiation of eq 14 leads to the relationship given in eq 16, which predicts a linear relation between

$$\Delta S^\circ = -(\partial\gamma/\partial T)\Delta G^\circ/(1 + \gamma) \qquad (16)$$

ΔG° and ΔS°, as do electrostatic models for ion–solvent interaction[3] and the Hammett equation as shown in the present eq 4. Christensen, Izatt, and Hansen[12] have plotted ΔG° vs. ΔS° for ionization of 103 carboxylic acids and we have done the same for a lesser number of phenols. Although a few acids are off the best straight lines by as much as 3 kcal/mol in ΔG° or 10 gibbs/mol in ΔS°, the predicted proportionality is observed for many acids.

We now differentiate eq 12 and combine with eq 14 and 16 to obtain eq 17. Since $\beta \cong T$, the terms in

$$\Delta C_p{}^\circ = \Delta S^\circ \left(\frac{\partial\beta}{\partial T} - 1\right)\left(1 - \frac{\beta}{T}\right) \qquad (17)$$

parentheses are both close to zero and we expect no well-defined relation between $\Delta C_p{}^\circ$ and ΔS°. Bell[13] has shown that an electrostatic model predicts $\Delta S^\circ = 1.7\Delta C_p{}^\circ$ and has noted that "there is no sign of any such regularity."

In summary we note that the present treatment (eq 11–17) leads to a general linear free-energy relation, accounts for the variation of ρ with temperature and allows ρ to depend on the solvent, predicts a propor-

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(3) E. J. King, "Acid–Base Equilibria," Pergamon Press, Oxford, 1965.
(4) L. G. Hepler and W. F. O'Hara, *J. Phys. Chem.*, **65**, 811 (1961).
(5) L. G. Hepler, *ibid.*, **68**, 2645 (1964).
(6) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **32**, 1333 (1936).
(7) R. F. Brown, *J. Org. Chem.*, **27**, 3015 (1962); R. F. Brown and H. C. Newson, *ibid.*, **27**, 3010 (1962).
(8) D. J. G. Ives and P. D. Marsden, *J. Chem. Soc.*, 649 (1965).
(9) C. D. Ritchie and W. F. Sager, "Progress in Physical Chemistry," Vol. 2, Interscience Publishers, Inc., New York, N. Y., 1964; C. D. Ritchie, Symposium on Linear Free Energy Correlations, Durham, N. C., 1964.
(10) H. H. Jaffé, *Chem. Rev.*, **53**, 191 (1953).
(11) P. R. Wells, *ibid.*, **63**, 171 (1963).

(12) J. J. Christensen, R. M. Izatt, and L. D. Hansen, *J. Amer. Chem. Soc.*, **89**, 213 (1967).
(13) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959.

tionality between $\Delta S°$ and $\Delta G°$ that has been observed for many acids, and accounts for the absence of correlation between $\Delta S°$ and $\Delta C_p°$.

The Preparation of 1,1-Diarylhydrazines

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In connection with some other work, pure 1,1-diphenylhydrazine was required in fairly large quantities. Although several routes are available for the preparation of 1,1-disubstituted dialkyl- and aralkylhydrazines, the reduction of the corresponding N-nitrosamine is practically the only general method for the synthesis of 1,1-diarylhydrazines.[1b]

In spite of its apparent relative simplicity, the reduction of 1,1-diphenylnitrosamine is always attended by cleavage of the N–N bond and the formation of diphenylamine.[2] The crude reaction product is usually a highly colored mixture of diphenylamine and of the desired hydrazine. The tedious purification yields more often than not 1,1-diphenylhydrazine hydrochloride as pale violet or silvery gray crystals at best, and, unless the purification is carried out carefully, substantial losses of product occur.

The experimental difficulties coupled with the rather prohibitive price of the commercial product (which is not pure) prompted us to investigate other routes to 1,1-diphenylhydrazine. One of the methods for the preparation of primary amines is the group of reactions which includes the Schmidt, the Hoffmann, and the Curtius rearrangement. Diaryl- and aralkylcarbamyl azides rearrange to give the corresponding N-isocyanates. Although this reaction has not been widely investigated,[3] the report by Scott and Scott[4] that 1,1-diphenylcarbamyl azide underwent the Curtius rearrangement in ethanol encouraged us to evaluate this as a potentially very useful and clean method to prepare 1,1-diarylhydrazines.

Three factors were of importance: high yields, ease of operations, and the purity of the hydrazines. Although it is known that primary alkyl esters of

$$\text{Ar}_2\text{NCOCl} + \text{NaN}_3 \longrightarrow \text{Ar}_2\text{NCON}_3 \xrightarrow{\text{ROH}}$$
$$\quad \text{I} \qquad\qquad\qquad\qquad \text{II}$$

$$\text{Ar}_2\text{NNHCO}_2\text{R} \xrightarrow{\text{H}_2\text{O}} \text{Ar}_2\text{NNH}_2$$
$$\qquad \text{III} \qquad\qquad\qquad \text{IV}$$

(1) (a) To whom all correspondence should be addressed. (b) P. A. S. Smith, "Open-chain Nitrogen Compounds," Vol. 2, W. A. Benjamin, Inc., New York, N. Y., 1966, p 144.

(2) E. Fischer, *Ann.*, **190**, 175 (1878); R. Stahel, *ibid.*, **258**, 243 (1890); C. Hanna and F. W. Schueler, *J. Amer. Chem. Soc.*, **73**, 4996 (1951); **74**, 3693 (1952); R. H. Poirier and F. Bennington, *ibid.*, **74**, 3192 (1952); S. Wexman, *Farm. Chilena*, **20**, 299 (1946); A. E. Arbuzov and F. G. Valitova, *J. Gen. Chem. USSR*, **27**, 2354 (1957); R. O. Matevosyan, *et al.*, *ibid.*, **31**, 3539 (1961); A. T. Balaban, *et al.*, *Tetrahedron*, **13**, 258 (1961).

(3) E. Lieber, R. L. Minnis, and C. N. R. Rao, *Chem. Rev.*, **65**, 377 (1965).

(4) F. L. Scott and M. T. Scott, *J. Amer. Chem. Soc.*, **79**, 6077 (1957).

carbamates are difficult to hydrolyze, the hydrolysis of ethyl 3,3-diphenylcarbazate[4] (III, Ar = Ph, R = C_2H_5-) was attempted under both acidic and basic conditions; in both cases the ester was recovered unchanged. However, the *t*-butyl ester (III, Ar = Ph, R = *t*-Bu-), in addition to the advantage of a shorter time for its preparation, was hydrolyzed easily to 1,1-diphenylhydrazine hydrochloride (IV·HCl) in 98% yield.

In order to evaluate its practical value for the preparation of 1,1-diphenylhydrazine, the sequence was carried through without purification of the intermediates. Thus, diphenylcarbamyl azide (II, Ar = Ph), mp 65°, obtained in 97% yield from the reaction of diphenylcarbamyl chloride and sodium azide, was heated under reflux with *t*-butyl alcohol for 5 days. The reaction was monitored by infrared spectroscopy and *t*-butyl 3,3-diphenylcarbazate (not isolated) was hydrolyzed with concentrated hydrochloric acid. 1,1-Diphenylhydrazine hydrochloride was obtained in 78% yield as *colorless* needles. Pure, *white* 1,1-diphenylhydrazine was isolated in 89% yield from its hydrochloride. The over-all yield of *pure* 1,1-diphenylhydrazine from diphenylcarbamyl chloride was 66%. In order to test the generality of this method, N-aminocarbazole was prepared and obtained as a pure solid in 74% yield (over-all) from biphenylenecarbamyl chloride.
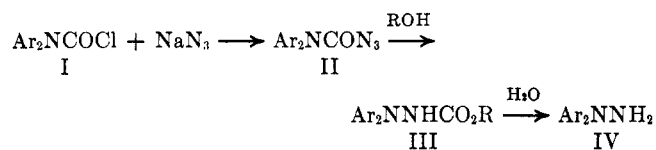
Except in cases when groups which are sensitive to the reagents used are present, this procedure should prove to be a widely useful method for the preparation of pure 1,1-diarylhydrazines. Although the decomposition of the azides and the subsequent reaction of the N-isocyanates with *t*-butyl alcohol takes about 5 days to be completed, the esters are stable and can be prepared in large quantities. The simple hydrolysis of the ester affords the pure hydrazine hydrochlorides in high yields.

Experimental Section[5]

N,N-Diphenylcarbamyl Azide.—A mixture of 23.2 g (0.1 mol) of diphenylcarbamyl chloride and 200 ml of ethanol contained in a 500-ml, round-bottom flask equipped with a reflux condenser was heated to 60°. As soon as solution had occurred, a solution of 6.5 g (0.1 mol) of sodium azide in 20 ml of water was added. The reaction mixture was heated under reflux with stirring for 3 hr. The ethanol was evaporated and 20 ml of water was added to the residue. The aqueous mixture was extracted with two 100-ml portions of ether. The dried ether extract was evaporated to give 23 g (97%) of diphenylcarbamyl azide, mp 65°. This compound was pure enough for the rearrangement reaction.

1,1-Diphenylhydrazine Hydrochloride.—A solution of 23 g of diphenylcarbamyl azide in 150 ml of *t*-butyl alcohol was heated under reflux for 5 days. After that time, the azide band (at 2160 cm^{-1}) had completely disappeared. A white solid, which was shown to be tetraphenylcarbohydrazide, mp 238°, by its infrared spectrum and a mixture melting point, was filtered. To the filtrate was added 10 ml of concentrated hydrochloric acid and the solution was heated under reflux for 3.5 hr. The residue left after removal of the solvent was washed with 50 ml of ether, and 1.3 g of *t*-butyl 3,3-diphenylcarbazate was obtained. The ether-insoluble *white* solid proved to be 1,1-diphenylhydrazine hydrochloride, mp 165–170°, and weighed 16.6 g (78%).

1,1-Diphenylhydrazine.—The hydrazine hydrochloride (19.3 g) obtained from the above procedure was dissolved in 500 ml of hot water and made strongly alkaline with 20 ml of a 7.5 *N* aqueous sodium hydroxide solution. The free hydrazine was