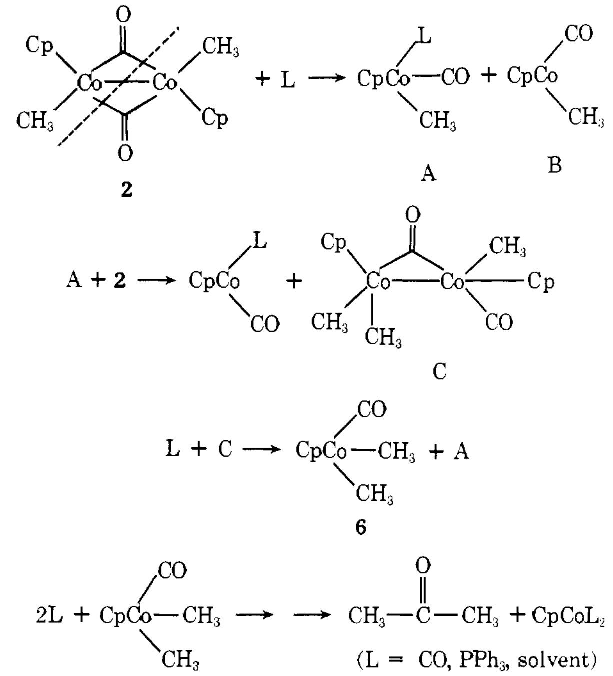
Scheme I



to give intermediate **6** and a molecule of A to continue the chain process.[12]

In conclusion, acetone formation from **2** is a very efficient process, but clearly occurs with concomitant cleavage of the metal-metal bond.[13] We are currently working on the preparation of complexes related to **2** having other alkyl groups; a comparison of their chemical behavior with that of **2** will be reported at a later date.

Acknowledgment. We are grateful to the National Science Foundation (Grant No. CHE-74-14711-AO2) and the National Institutes of Health (Grant No. GM-16231) for financial support of this work.

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(4) The chromatography was carried out inside a Vacuum Atmospheres recycling inert atmosphere box (N_2 atmosphere). Using benzene as eluent, R_f(**2**) = 0.56; other materials formed in this reaction and collected without decomposition from the column were η^5-$C_5H_5Co(CO)_2$ (R_f = 0.61) and (η^5-$C_5H_5CoCO)_3$ (R_f = 0.42).

(5) (a) C and H analyses were performed by Dr. S. Rottschaefer in the Caltech Analytical Laboratory. Cobalt analyses were carried out by Galbraith Laboratories, Knoxville, Tenn. Cryoscopic molecular weights were measured by Dornis u. Kolbe Microanalytisches Laboratorium, Mülheim, Germany. (b) We cannot at present rule out the possibility that the methyl groups are bridging rather than terminal; see, e.g., E. O. Fischer, et al., *Angew, Chem., Int. Ed. Engl.*, **12**, 943 (1973).

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(9) We have recently found that the known,[10] stable phosphine complex **5**, under 1 atm of CO in THF, gives a quantitative yield of acetone and η^5-$C_5H_5Co(CO)_2$ under the influence of UV irradiation (at 25 °C) or heat (~70 °C). Complex **8** is a detectable intermediate (NMR) in the photochemical reaction (E. Evitt and R. G. Bergman, unpublished observations).

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(11) The complex formed in greatest amount is the thermodynamically most stable material [η^5-$C_5H_5Co(CO)(PPh_3)$], which suggests that the yields of these materials may not reflect the kinetic product distribution of the phosphine induced reaction. This possibility is currently under investigation.

(12) Short-lived intermediates such as A and C may, of course, avoid 19-electron metal configurations by temporarily reducing the number of electrons donated by the η^5-C_5H_5 ligands. When L = solvent (no PPh_3 or CO present), $CpCoL_2$ and CpCo(CO)L are not stable and decompose to the cluster complexes observed as final products.

(13) Two somewhat related reactions are worthy of mention here. In the first, $[Ru(CO)_4SiMe_3]_2$ has been prepared[13a] and shown to undergo PPh_3-induced decomposition to $(PPh_3)_2Ru(CO)_3$ and $(PPh_3)_2Ru(CO)_2(SiMe_3)_2$. Later work has shown[13b] that the kinetics of this process are consistent with an initial reversible metal-metal bond cleavage step followed by coordination of a ligand (a similar overall process is shown as the first line of Scheme I). The second reaction is the decomposition of the cobalt(I) complex $CH_3Co(CO)_4$; although no yields are reported, acetone appears to be the only volatile organic product of this reaction.[13c,d] In contrast to the behavior of cobalt(II) complex **2**, however, the presence of free CO appears to *inhibit*, rather than accelerate, the formation of ketone;[13d] and $CH_3COCo(CO)_4$ is observed instead; (a) S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc. A*, 2559 (1969); (b) U. P. Fawcett, A. J. Pöe, and M. V. Twigg, *J. Organomet. Chem.*, **51**, C17 (1973); (c) W. Hieber, W. Beck, and E. Lindner, *Z. Naturforsch. B*, **16**, 229 (1961); (d) W. Beck and R. E. Nitzschmann, *Chem. Ber.*, **97**, 2098 (1964).

(14) National Institutes of Health Postdoctoral Research Fellow, 1975-1976.

(15) National Institutes of Health Postdoctoral Research Fellow, 1974-1975.

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Calculation of Polar Substituent Parameters by ab Initio Molecular Orbital Methods. Proton Affinities of Substituted Primary Amines[1]

Sir:

Progress toward the interpretation of structure-energy relationships in physical organic chemistry has been greatly aided by the evolution of techniques for the precise measurement of equilibrium constants for proton transfer reactions in the gas phase,[2,3] and by the development of simple nonempirical molecular orbital methods [4]with which it is possible to reliably calculate the energies of such processes. The widespread use of linear free energy relationships based upon standard proton transfer reactions in aqueous solution has been tempered (or even made hazardous) in fundamental understanding by aqueous solvent effects now known to range up to $\sim 10^{40}$ for proton transfer between neutral bases.[5]

Gas phase proton transfer equilibria between meta- and para-substituted benzoic acids have been correlated with σ^0 values;[6] proton transfer equilibria between para-substituted α-methyl styrenes and between para-substituted benzaldehydes even more closely follow σ^+ parameters.[7] Thus, for "chemically inert" type substituents in the benzene system, solvent may strongly attenuate the substituent effect (factors of 2-10 have been reported[3]), but the nearly fixed order of substituent effects is maintained in the gas phase and in aqueous solution.

We report here the results of the first study of the relationship of gas phase proton transfer equilibria and the polar substituent parameters, σ_I. Gas phase proton transfers between β-substituted ethylamines are ideally suited *in part* to definitive determinations of polar effects of substituents in the absence of solvent. This follows from the relatively simple nature of the strongly basic functional group; i.e., both free base and conjugate acid involve the single atomic (N) position with classically saturated (nonconjugating) structures and nearly the same hybridization. However, conformational effects (i.e., chelation), arising because of the flexibility of the molecular skeleton,[8] complicate the use of the β-substituted ethylamines for this purpose. This situation is compounded in the gas phase by the polarizability effect[2e,3,9] (i.e., preferential stabilization of BH^+ by the interaction of the charge with the polarizable substituent and molecular framework) as well as effects of internal H-bond chelation between substituent and the am-

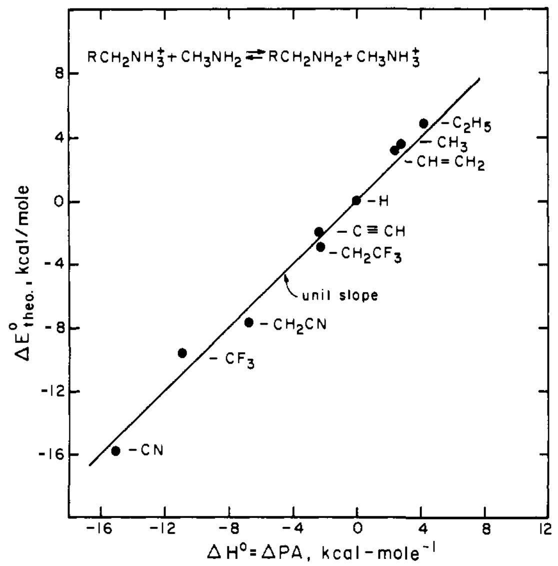


Figure 1. ΔE°_{theo} vs. ΔH° for proton transfer reactions: ordinate.

monium ion center.[3,10] Both of these effects offer potential major contributions to the measured substituent effects on the proton affinities of β-substituted ethylamines. That is, polar substituent effects alone (arising in the simple electrostatic model from ion-dipole interactions) cannot be obtained quantitatively from the measured proton affinities of a series of β-substituted ethylamines because of these additional contributions.

The theoretical approach offers an advantage, in that it is often possible to separate the effect of interest from other complicating effects. A recent example is the calculation of substituent effects on the proton affinity of benzene.[11] Experimental values of these proton affinities are complicated by variable (uncertain) sites of protonation, i.e., the four different ring positions or a position within the substituent itself.[12] The calculations avoid this nontrivial experimental complication and have been carried out for the formation of an extended series of meta- and para-substituted benzenium ions using the minimal basis set STO-3G method. The results have provided a theoretical scale of σ^+ parameters.[11]

In a similar usage to obtain a theoretical scale of σ_I (polar) substituent parameters, the proton affinities of substituted primary amines provide a critical ingredient which was unavailable for the substituted benzenes. That is, good quantitative agreement between calculated and experimental values[2e,3,13] of relative proton affinities can be shown for the substituted amines, which involve a complex combination of polar, polarizability, and conformational effects. With this assurance, one can with confidence proceed to use the theoretical calculations, with the needed molecular constraints, to estimate quantitatively the scale of polar substituent effects from the relative proton affinities for β-substituted ethylamines.

In Figure 1 are plotted experimental vs. theoretically calculated[14] relative proton affinities for substituted primary amines relative to methylamine, i.e., ΔH° for the reaction $RCH_2NH_3^+ + CH_3NH_2 \rightleftharpoons RCH_2NH_2 + CH_3NH_3^+$. The average deviation from unit slope in Figure 1 is ± 0.8 kcal mole for eight substituents covering a range of 19.4 kcal.

By restricting both β-substituted ethylamines and their conjugate acids to a fully extended (all trans) molecular conformation, effects of chelation and perhaps of other attractive or repulsive conformational variances are eliminated from the calculated proton transfer energies. In addition, distance and structure factors are such as to minimize contributions form polarizability and hyperconjugation effects. That is, the energy change calculated by the STO-3G minimal basis set method for the following hypothetical reaction provides quantitative estimates of the effects of polar substituents, R, in the absence

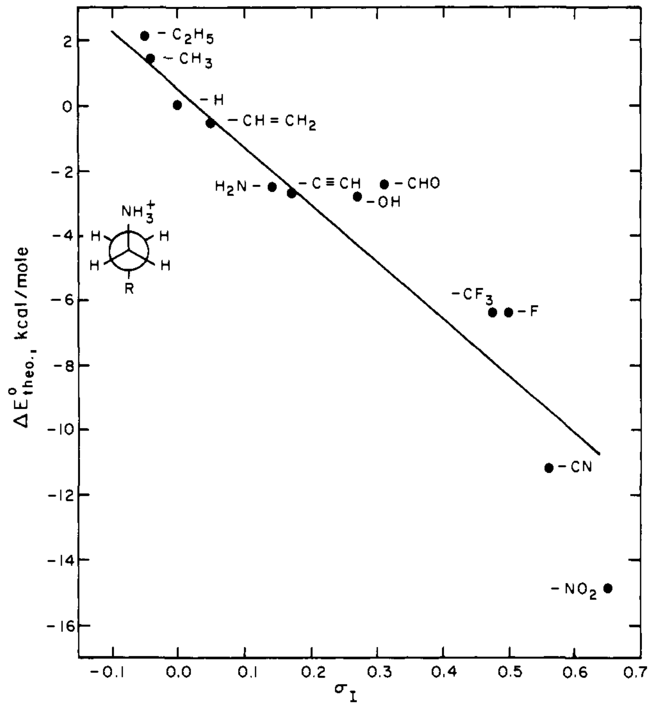
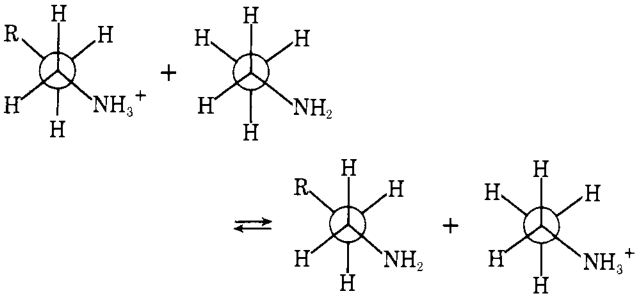


Figure 2. ΔE°_{theo} vs. σ_I. Extended (all trans) β-substituted ethyl amines.



of solvent. Figure 2 shows a plot of the calculated polar substituent effects vs. the empirical σ_I parameters[19] for these effects. Omitting the NO_2 point, the ρ value of +12.9 obtained from Figure 2 (slope converted to log $(K_{BH^+}/K_{B_0H^+})/\sigma_I$) is in reasonable accord with the value (+10) obtained by Taft for the relative gas phase proton affinities of a necessarily limited series of polar substituted $XCH_2N(CH_3)_2$ amines, utilizing a "conversion" factor of 2.4 found applicable to these two series of gas phase proton transfer equilibria.[3] The scatter of points in Figure 2 is such that it cannot be ascribed alone to medium effects on the empirical σ_I scale, although such effects may obviously contribute (e.g., CHO[20]). Some secondary effects (real or artifacts) in the theoretical calculations are evidently also involved. The result for the NO_2 substituent in particular seems to give too large a base weakening effect. However, the results illustrated in Figure 2 satisfactorily confirm the basic concepts which have been associated with the empirical σ_I scale of substituent polar effects. Clearly, the first step of the way has been paved for definitive tests which will follow of the proposed separation[21] of intrinsic polar and resonance effects of substituents in the aromatic series. Experimental and theoretical work on proton affinities is in progress also with much more rigid saturated molecular cavities, e.g., the quinuclidine and bicyclooctane [2.2.2] frameworks, which will offer further evidence on the scale of intrinsic polar substituent effects.

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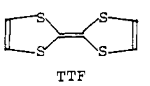
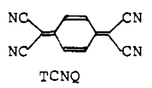
Photodesulfurization by Distannane. Photochemical Synthesis of Tetrathiofulvalenes

Sir:

The recent discovery[1] of highly conductive organic charge transfer complexes which are formed from derivatives of tetrathiofulvalene (TTF) and the acceptor molecule, tetracyano-*p*-quinodimethane (TCNQ), has stirred interest in the discovery of a new synthetic method for TTF derivatives.[2]



TTF



TCNQ

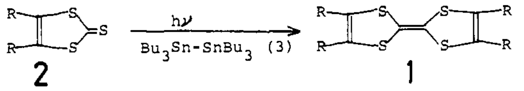
In connection with our previous work[3] on TTF and related compounds, we have investigated the one-step synthesis of TTF derivatives from 1,3-dithiole-2-thiones.

Table I. Photosynthesis of TTF derivatives **1**[a]

	2 R	(mmol)	**3** (mmol)	Solvent[b] (ml)	Yield of **1**[c] (%)	
2a	Me	0.5	0.5	H (18)	**1a**	56
2a	Me	0.5	1.0	H (18)	**1a**	77
2b	$\leftarrow CH_2 \rightarrow_2$	0.5	0.5	B (18)	**1b**	68
2c	COOMe	1.0	1.0	H-B (15-15)	**1c**	73
2d	Ph	0.5	0.5	H-B (5-10)	**1d**	50

[a] Reaction time is 5 h except **2d** (24 h). [b] H, hexane; B, benzene. [c] The yields have not been optimized in any case.

We wish to report here the first example of photochemical synthesis of the title compounds, using distannane. The procedure involves irradiation of 1,3-dithiole-2-thiones (**2**), in the presence of hexabutyldistannane (**3**), to give the corresponding TTF derivatives **1** in good yields.



The method has proven to be superior to the base catalyzed dimerization of 1,3-dithiolium ions, the method[4,5] initially used to synthesize TTF. The method also appears to be a more general preparation of TTF derivatives substituted with either electron-donating or -withdrawing groups.[6]

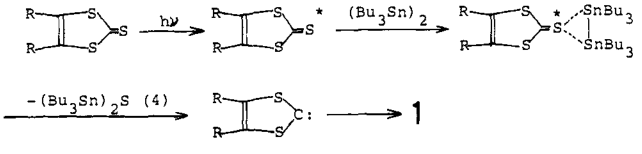
The general procedure is as follows. A benzene or hexane solution of an equimolar amount of **2**[5,6] and distannane **3**[7] in a quartz tube cooled by water was irradiated with a 300-W high-pressure mercury lamp for 5 h. After removing the solvent under reduced pressure, the residue was treated with a small amount of pentane to precipitate crystals of **1** (**1a, b, d**), or purified by column chromatography (alumina, benzene-EtOAc) (**1c**). The structure of the products was confirmed by comparison of their physical and spectral properties with those of authentic samples or with the data reported in the literature.[3,5,6]

As shown in Table I, a higher yield of **1a** was obtained when twice the molar amount of distannane **3** was employed.

Since there are very few reports on the photochemistry of distannane,[8] we have examined the photochemical behavior of distannane, which provided the following observations: (1) In the absence of **3**, or without irradiation, no reaction was observed. (2) TTF derivatives, **1**, were not obtained in the thermal reaction of **2** and **3** in the presence of azobisisobutyronitrile (AIBN) which was expected to cleave the tin-tin bond of distannane **3**.[8] (3) Bis(tributyltin) sulfide (**4**)[9] was isolated by column chromatography. (4) Hexabutyldistannane (**3**) apparently showed no absorptions in the uv and visible regions (210–700 nm). (5) The rate of the photoreaction varies with the wavelength of irradiating light. The relative rate of the second-order reaction of **2a** and **3** in cyclohexane at ca. 20 °C was estimated by monochromic irradiation (Table II).

The rate enhancement was observed at wavelengths especially in the uv range, which correspond to the absorptions of **2a**.

These facts suggest a possible reaction scheme as shown below.



The initial homolytic cleavage of the tin–tin bond is unlikely as a key step because of the ineffectiveness of AIBN. Instead,