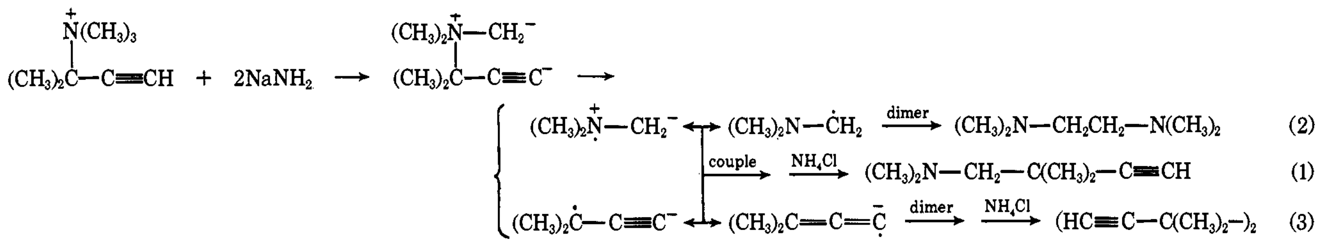

chloride (40 g, 0.75 mol), ether (500 ml), ice (300 g), and water (200 ml) gave three products indicative of Stevens rearrangement by a homolytic cleavage–recombination mechanism.

Extraction of the ethereal solution (ammonia removed by partial distillation of ether) with cold 0.6 N HCl and release of amines with 3.0 N NaOH gave an oil shown by glpc to contain 8.1 g (24% yield) of 3,3-dimethyl-4-dimethylamino-1-butyne (**1**) and 0.6 g (4% yield) of N,N,N′,N′-tetramethylethylenediamine (**2**). Separation was achieved by preparative glpc (20% THEED on 60–80 Chromosorb P (base washed) at 90°; 18 ft × $^3/_8$ in. column; helium flow 40 cc/min). The rearrangement product (**1**) had bp 116–117°; $n^{25}\text{D}$ 1.4180; ir 3333 and 2105 (C≡CH), 1385 and 1355 cm^{-1} ($C(CH_3)_2$); nmr (neat) δ 1.14 (s, 6, $(CH_3)_2C$), 2.07 (s, 1, C≡CH), 2.22 (s, 2, $C\text{–}CH_2\text{–}N$), and 2.30 (s, 6, $N(CH_3)_2$). The hydrochloride salt had mp 198–200°. *Anal.* Calcd for $C_8H_{16}ClN$: C, 59.43; H, 9.98; N, 8.66. Found: C, 59.24; H, 9.85; N, 8.88. Identification of **2** was made by comparison of physical and spectral properties with those of an authentic sample and with literature data.[3]

The original ether layer (amines removed) was washed with 10% Na_2CO_3, dried, and distilled to yield 1.3 g (twice distilled, 7.2% yield) of 3,3,4,4-tetramethyl-1,5-hexadiyne (**3**), bp 55–60° (50 mm) and 133–134° (capillary method); $n^{25}\text{D}$ 1.4416; ir 3300 and 2110 cm^{-1} (C≡CH); nmr (CCl_4) δ 1.99 (s, C≡CH) and 1.33 (s, CH_3) in the ratio 1:6. *Anal.* Calcd for $C_{10}H_{14}$: C, 89.49; H, 10.51. Found: C, 89.75; H, 10.24.

The following mechanism is suggested to account for the three reaction products. It is worthy of note that ionic cleavage would have given the zwitterion carbene, $(CH_3)_2C^+\text{—}C{\equiv}C^- \leftrightarrow (CH_3)_2C{=}C{=}C{:}$, as an intermediate, providing a route to 3-amino-3-methyl-1-butyne by reaction with the ammonia solvent.[4] No trace of the latter compound could be found among the reaction products.

Although Schöllkopf, *et al.*,[1c] observed dibenzyl as a minor (5%) by-product in the rearrangement of benzyldimethylphenacylammonium ylide, formation of *three* possible radical coupling products has not been reported previously. The recent claims[1] for homolytic cleavage–recombination mechanisms were supported mainly by observations of chemically induced dynamic nuclear polarization.

Acknowledgments. The senior author acknowledges a stimulating discussion with Professor Albert Eschenmoser at Notre Dame on March 15, 1968, in which A. E. suggested that Stevens and Sommelet–Hauser rearrangements of *t*-propargylic quaternary ammonium salts then under initial investigation might involve ion-radical intermediates. The financial support of this work by Eli Lilly and Company, Indianapolis, Ind., is gratefully acknowledged.

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[3] L. Spialter and J. A. Pappalardo, "The Acyclic Aliphatic Tertiary Amines," Macmillan Company, New York, N. Y., 1965, p 351.

[4] G. F. Hennion and E. G. Teach, *J. Amer. Chem. Soc.*, **75**, 1653 (1953); G. F. Hennion and J. F. Motier, *J. Org. Chem.*, **34**, 1319 (1969).

Substituent Effects in the Formation of Some Protonated Ketones and the Corresponding Carbonium Ions[1,2]

Sir:

When the heats of protonation ($\Delta\bar{H}_{a,b}$)[1b] of a series of benzophenones are determined in fluorosulfuric acid,[3] a substituent effect is found (Table I). Realizing that this observation bears on the question of charge distribution in protonated ketones, we have determined the heats of protonation for the corresponding 1,1-diarylethylenes.[4]

The quantitative formation of diarylmethylcarbonium ions from diarylethylenes in strong acids is one of the most thoroughly documented processes in physical organic chemistry.[5,6] The effects of substituents on it may be considered as a calibration scale for evaluating charge delocalization in diarylcarbonium ions. In the present experiment, the carbonium ions and corresponding protonated ketones are formed through similar processes under identical conditions and so are free of the interpretive problems normally encountered when acidity function extrapolations are used to obtain comparable free energy data at a common standard state.

Heats of protonation ($\Delta\bar{H}_{a,b}$) listed in Table I represent heats of transfer from high dilution in carbon tetrachloride (the reference state) to high dilution in fluorosulfuric acid, $\Delta\bar{H}_{a,b} = \Delta\bar{H}_{HSO_3F} - \Delta\bar{H}_{CCl_4}$. The calorimetric method used here has been described pre-

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[1] (a) Weak Bases in Strong Acids. V. (b) Previous paper in this series: E. M. Arnett, J. J. Burke, and R. P. Quirk, *J. Amer. Chem. Soc.*, in press.

[2] Supported by National Science Foundation Grant GP-6550X.

[3] E. M. Arnett, J. W. Larsen, and R. P. Quirk, *J. Amer. Chem. Soc.*, in press.

[4] Protonation of 1,1-diarylethylenes appeared to us to be a particularly good model for protonation of benzophenones. The parent compounds have very similar structures so that the protonations should involve similar entropic contributions. The diarylmethylcarbonium ion which results from protonation of the 1,1-diarylethylenes bears a strong formal resemblance to the hydroxycarbonium ion resonance form which may be written for the protonated benzophenones except for differences between the ability of the CO^+H and the C^+CH_3 groups to be stabilized by hydrogen bonding to the solvent.

[5] G. A. Olah, *J. Amer. Chem. Soc.*, **86**, 932 (1964).

[6] (a) N. C. Deno, P. T. Groves, and B. Saines, *ibid.*, **81**, 5790 (1959); (b) M. T. Reagan, *ibid.*, **91**, 5506 (1969); (c) G. A. Olah, *et al.*, *ibid.*, **88**, 1488 (1966); (d) V. Gold and F. L. Tye, *J. Chem. Soc.*, 2172, 2184 (1952); (e) J. A. Grace and M. C. R. Symons, *ibid.*, 958 (1959); (f) V. Gold, B. W. V. Hawes, and F. L. Tye, *ibid.*, 2167 (1952); (g) A. G. Evans, *J. Appl. Chem.*, 1, 240 (1951); (h) H. P. Leftin in "Carbonium Ions," Vol. I, G. A. Olah and P. von R. Schleyer, Ed., Interscience Publishers, New York, N. Y., 1968, p 353.

Table I. Heats of Protonation of Substituted Benzophenones and 1,1-Diarylethylenes in HSO_3F at 25°

Substituent		$-\Delta\bar{H}_{HSO_3F}$, kcal/mol	$\Delta\bar{H}_{CCl_4}$, kcal/mol	$-\Delta\bar{H}_{a,b}$, kcal/mol	$-pK^c$
4-Methoxy	*a*	14.1 ± 0.1	6.1 ± 0.2	20.2 ± 0.2	
	b	17.1 ± 0.1[d]	6.6 ± 0.1	23.7 ± 0.1	
4,4′-Dimethyl	*a*	12.6 ± 0.2	5.5 ± 0.1	18.1 ± 0.2	5.8
	b	13.5 ± 0.2	5.6 ± 0.3	19.1 ± 0.4	9.1
4-Methyl	*a*	12.9 ± 0.2	4.9 ± 0.2	17.8 ± 0.3	
	b	15.9 ± 0.1	0.0 ± 0.1	15.9 ± 0.1	
Unsubstituted	*a*	11.6 ± 0.2	5.3 ± 0.2	16.9 ± 0.3	6.4
	b	14.6 ± 0.2	0.1 ± 0.07	14.7 ± 0.2	10.4
4-Chloro	*a*	10.2 ± 0.4	5.4 ± 0.2	15.6 ± 0.4	6.9
	b	12.7 ± 0.2	0.6 ± 0.2	13.3 ± 0.3	
4-Bromo	*a*	9.6 ± 0.3	5.5 ± 0.4	15.1 ± 0.5	
	b	13.6 ± 0.2	0.3 ± 0.1	13.9 ± 0.2	
4,4′-Dichloro	*a*	8.5 ± 0.2	6.4 ± 0.1	14.9 ± 0.2	7.3
	b	6.7 ± 0.3	6.4 ± 0.2	13.1 ± 0.4	11.4
4,4′-Dimethoxy	*a*	21.5 ± 1.5[d]	8.6 ± 0.5	30.1 ± 1.8	4.5
	b	28.8 ± 0.4[d]	7.7 ± 0.2	36.5 ± 0.5	5.5

[a] Benzophenone values. [b] 1,1-Diarylethylene values. [c] pK_{BH^+} values for benzophenones are from R. Stewart, *et al.*, *Can. J. Chem.*, **41,** 1065 (1963), corrected to the H_0 scale of M. J. Jorgenson and D. R. Hartter, *J. Amer. Chem. Soc.*, **85,** 878 (1963); pK'_{R^+} values for 1,1-diarylethylenes are from ref 6b. [d] See ref 7.

viously.[3] All compounds had physical constants in good agreement with literature values, and the purity of liquids was checked by glpc. Clean nmr spectra authenticating simple protonation were observed for most[7] of the compounds in both series in fluorosulfuric acid at solute concentrations from 0.1 to 1.0 *M*, at 35–40°.

Plots of $\Delta\bar{H}_{a,b}$ *vs.* σ^+[8] for the benzophenones and 1,1-diarylethylenes (Figure 1) have least-squares slopes of 4.59 (s_m = 0.67, r = 0.95) and 6.75 (s_m = 0.84, r = 0.97), respectively.[9] The spacings of relative enthalpies of protonation are thus fully $^2/_3$ as large in the benzophenone series as in the 1,1-diarylethylenes indicating that considerable delocalization of charge from the protonated oxygen is possible when structural requirements are met.[10]

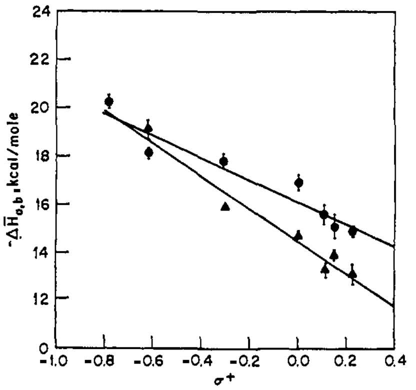

Figure 1. Plots of $\Delta\bar{H}_{a,b}$ *vs.* σ^+ for benzophenones (●) and 1,1-diarylethylenes (▲).

Correlations of these enthalpies of protonation with available pK'_{R^+} or pK_{BH^+} values[11] are illustrated in Figure 2.[12]

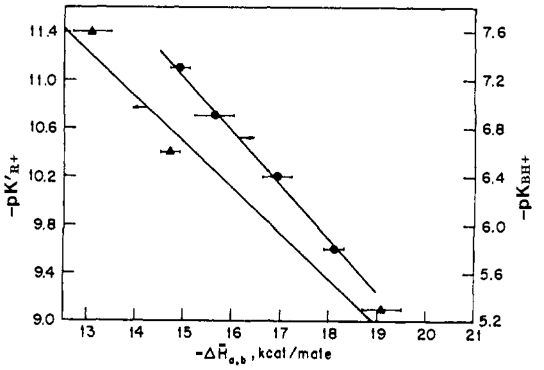

Figure 2. Plots of $\Delta\bar{H}_{a,b}$ *vs.* p*K* for benzophenones (●) and 1,1-diarylethylenes (▲). See Table I for sources of p*K* values.

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(7) The nmr spectra of protonated 4,4′-dimethoxybenzophenone, 1,1-bis(4′-dimethoxyphenyl)ethene, and 1-phenyl-1-(4′-methoxyphenyl)ethene indicate that the solvent reacts with the methoxyphenyl group(s) in these molecules; thus, their anomalously large heats of protonation have not been used in arriving at the conclusions reached herein. Nitro groups were avoided since they are known to interact with this solvent (see ref 4 and references cited therein).

(8) No significance should be attached to our use of σ^+ over σ since for these substituents σ and σ^+ constants form a good straight line when plotted against each other.

(9) Formulae from D. C. Baird, "Experimentation: An Introduction to Measurement Theory and Experiment Design," Prentice-Hall, Inc., Englewood Cliffs, N. J., 1962, were used to compute the slopes, their standard deviations (s_m), and correlation coefficients (r).

(10) $\Delta\bar{H}_{a,b}$ represents the difference in enthalpy between the free base and protonated states, so that substituent effects on initial states in both series must be considered. As relevant analogs, Taft and coworkers [*J. Amer. Chem. Soc.*, **87**, 2489 (1965); **89**, 2391 (1967)] have compared the charge delocalization by *p*-^{19}F nmr measurements of substituted triarylcarbonium ions and protonated benzophenones. Taft has informed us that a linear plot for eleven substituents in the two series has a (C^+/CO^+H) slope of 1.33 compared to 1.47 (6.75/4.59) found by us here. Giam and Taft (and McKeever) [*ibid.*, **89**, 2397 (1967)] have concluded that substituent effects in the triarylcarbinol-carbonium ion equilibrium lie about 97% in the cation. Our interpretations of $\Delta\bar{H}_{a,b}$ in terms of delocalization energies of the ions assume that substituent effects on the relative enthalpies of unprotonated benzophenones and 1,1-diarylethylenes will be similar enough so that differences in $\Delta\bar{H}_{a,b}$'s can be thought of strictly in terms of the protonated species. We understand that Taft plans to test this assumption by his ^{19}F nmr approach.

(11) Reliable basicities of carbonyl compounds are difficult to obtain;[4] therefore, it should be emphasized that these pK_{BH^+} values were all measured in the same laboratory (see Table I) and thus are no doubt internally consistent. The good linear correlation noted between $\Delta\bar{H}_{a,b}$ and $\Delta G_i°$ for protonation of various aryl compounds by E. M. Arnett and J. W. Larsen, *ibid.*, **90**, 792 (1968), is further evidence that enthalpy may parallel free energy in systems of this kind.

(12) Reagan's[6b] value for 1-phenyl-1-(4′-methoxyphenyl)ethene fits the pK'_{R^+} *vs.* $\Delta\bar{H}_{a,b}$ plot (by either adjusting his value to the H_R' scale or Deno's values to the H_C scale) but since our nmr evidence indicates that processes other than simple protonation occur when this compound reacts with fluorosulfuric acid we have not included the point in this figure. Also, it should be noted that in Figure 1 the point for this compound would fall more than four standard deviations from the line described by the other six 1,1-diarylethylenes.

Previous reports on the electronic structure of protonated ketones vary in their terminology, but the spectroscopic results are by now generally consistent with each other and with the conclusions presented by us. In a series of papers, Olah and coworkers[13] report nmr studies of protonated alicyclic and aliphatic ketones and protonated aldehydes. On the basis of CO^+H proton signals at very low fields, they originally considered the protonated ketones studied by them to be represented best as oxonium ions ($>C{=}O^+H$), the alternative hydroxycarbonium ion valence bond form ($>C^+{-}OH$) being of lesser importance in the resonance hybrid. However, their more recent ^{13}C work indicates variation of charge delocalization as a function of the carbonyl base. Deno[14] considers the hydroxycarbonium ion form of protonated ketones to be a significant contributor to the resonance hybrid, based on comparison of the uv spectra for a series of protonated unsaturated and aromatic ketones with their corresponding carbonium ions. Brouwer[15] has used the terms "hydroxycarbonium ion" and "protonated ketone" interchangeably in his recent nmr study of protonated dialkyl ketones. Based on the observation that δ CO^+H in $R_1R_2CO^+H$ varies by 5 ppm (11–16 ppm), Levy and Winstein[16] adopted the view that charge distribution may be varied from largely oxonium ion to almost completely hydroxycarbonium ion[17,19] by changing the substituents on the carbonyl group. This viewpoint is supported by the observation that the energy barrier to interconversion about a protonated or alkylated carbonyl bond is quite sensitive to the electron-donating ability of the rest of the molecule.[21,22] A comparison of δ CO^+H values with $\Delta\bar{H}_{a,b}$ for benzophenone (12.23 ppm,[20] -16.9 kcal/mol), 4-chlorobenzophenone (12.50 ppm,[18] -15.6 kcal/mol), and 4-bromobenzophenone (12.60 ppm,[18] -15.1 kcal/mol) shows a trend of decreasing chemical shift with increasing exothermicity. Such a correlation might be anticipated in light of Birchall and Gillespie's finding[23] that δ CO^+H for *para*-substituted acetophenones gives linear correlations with σ^+ and pK_{BH^+}. It has been recognized,[4] however, that there is no single correlation between δ CO^+H and $\Delta\bar{H}_{a,b}$ for all types of ketones (aromatic, aliphatic, etc.).

The work described here provides thermodynamic information for a case where structural conditions favoring resonance delocalization of charge in the protonated species have been optimized. We have found a close similarity of the response to substituent change for the two protonation reactions as manifested by the order and magnitude of $\Delta\bar{H}_{a,b}$. This suggests strongly a similar mode of charge delocalization in both series of ions.

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[13] (a) C. U. Pittman, Jr., and G. A. Olah, *J. Amer. Chem. Soc.*, **87**, 5123 (1965); (b) G. A. Olah, D. H. O'Brien, and M. Calin, *ibid.*, **89**, 3582 (1967); (c) G. A. Olah, M. Calin, and D. H. O'Brien, *ibid.*, **89**, 3586 (1967); (d) G. A. Olah and M. Calin, *ibid.*, **90**, 938 (1968); (e) G. A. Olah and A. M. White, *ibid.*, **91**, 5801 (1969).

[14] N. C. Deno, *Progr. Phys. Org. Chem.*, **2**, 182 (1964).

[15] D. M. Brouwer, *Rec. Trav. Chim. Pays-Bas*, **86**, 879 (1967).

[16] G. C. Levy and S. Winstein, Abstracts of Papers, 158th National Meeting of the American Chemical Society, New York, N. Y., 1969, ORGN 111.

[17] Sekuur and Kranenburg[18] have reported δ CO^+H values for several substituted benzophenones in $SbF_5{-}HSO_3F$ at low temperature. They range from 12.47 (4,4′-dibromo) to 13.70 (2,4,5-trimethyl) ppm downfield from TMS, intermediate between the extremes noted by Levy and Winstein.

[18] Th. J. Sekuur and P. Kranenburg, *Tetrahedron Lett.*, **39**, 4793 (1966).

[19] Hogeveen [H. Hogeveen, *Rec. Trav. Chim. Pays-Bas.*, **86**, 696 (1967)] reports δ CO^+H of 15.13 ppm for acetone in $HF{-}BF_3$ at $-80°$; this resonance is reported to occur at 14.24 ppm in a 9:7:2 molar $SO_2{-}FSO_3H{-}SbF_5$ mixture at $-59°$.[20] Thus, medium effects on these chemical shifts can be substantial.

[20] M. Brookhart, G. C. Levy, and S. Winstein, *J. Amer. Chem. Soc.*, **90**, 1735 (1968).

[21] M. Brookhart, Ph.D. Thesis, U.C.L.A., 1968.

[22] Taft [B. G. Ramsey and R. W. Taft, *J. Amer. Chem. Soc.*, **88**, 3058 (1966)] reports a free energy barrier to interconversions in the dimethoxymethyl cation of 15 kcal/mol and estimates a π-bond order of 0.2–0.3 for the $C^+{-}O$ bonds in this ion.

[23] T. Birchall and R. J. Gillespie, *Can. J. Chem.*, **43**, 1045 (1965).

Photolysis of Benzaldehyde in Solution Studied by Nuclear Magnetic Resonance Spectroscopy

Sir:

We wish to report evidence which indicates that the photolysis of benzaldehyde in solution leads to a radical pair as one of the reaction intermediates. This evidence was obtained by measuring the nmr spectrum of ground-state benzaldehyde and its products during optical irradiation. This technique has been employed previously to study anthraquinone in its excited triplet state,[1] and the details will not be repeated here. In essence, this technique enables one to detect short-lived paramagnetic intermediates (species with unpaired electrons) which, although they exist in very low concentrations, can be observed because the unpaired electrons strongly polarize the nuclear spins. This polarization is retained when the intermediate is converted to a stable diamagnetic state such as the ground state of the starting material or products. Because the nuclear spin states have populations different from those expected for a Boltzmann distribution,[2] the nmr spectrum contains enhanced absorption and emission lines.[1,3]

For benzaldehyde, the resulting spectra are given in Figure 1. Figure 1a gives the spectrum of benzaldehyde in perdeuteriobenzene at 25° before optical irradiation. The field increases from left to right, and this spectrum is a time average of 12 scans. Figure 1b, which is a time average of two scans, illustrates the spectrum of the same solution obtained during irradiation with 2000–4000-Å light. Since Figure 1b represents fewer scans than Figure 1a, it is clear that both the aldehyde and ring proton nmr lines are enhanced during optical irradiation and that the enhancement is larger for the aldehyde proton. This enhancement appears as soon as the irradiation is started. In addition one line appears at higher field as an emission line. When optical irradiation is stopped, all of the lines relax in less than 10 sec to absorption lines having substantially lower intensities than the lines observed during irradiation.

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[1] M. Cocivera, *J. Amer. Chem. Soc.*, **90**, 3261 (1968).

[2] A. Abragam, "The Principles of Nuclear Magnetism," Oxford University Press, London, 1961.

[3] Other workers have been able to study thermally generated free-radical intermediates in a similar manner by measuring the nmr of the stable products resulting from these free radicals. For a brief review, see H. Fischer and J. Bargon, *Accounts Chem. Res.*, **2**, 110 (1969).