Excited state calculations were then performed in the singly excited configuration-interaction approximation[23] with inclusion of a large number (~70) of configurations to obtain the excited state energies and oscillator strengths for the singlets in the dipole length approximation, including one-center sp terms,[24] consistent with the INDO model. The results on **1a** and **8** are shown in Table I.

The calculated states and their energies are in good agreement with observed spectroscopic properties, the estimate of E_T from the quenching experiments on **8**, and the commonly accepted singlet-triplet energy splittings for n → π^* transitions (0.4 eV).[27] Some results from CNDO/S calculations on **1a** and **8** have recently been published by Houk et al.[9,28] Although details about the calculations and results were not given, some of their results and conclusions are in apparent disagreement with our present calculations and need reinterpretation. It was stated[9] that T_1 was π,π^* for **1a** and n,π^* (or CT) for **8**, and that the relative energies of the states of these systems were "extremely sensitive" to symmetry and substituents. The calculations[9] were used to explain apparent variations in singlet and triplet photochemistry as well as intersystem crossing efficiencies in 3,5-cycloheptadienones, in agreement with the reported[10] photochemistry of **8**, which we now have shown to be largely incorrect, especially with respect to singlet reactivity. In contrast, our calculations show a striking similarity in both the energies and contributions of configurations of all low-lying singlet and triplet states of **1a** and **8**.

Our calculations are useful in interpreting the observed photochemistry of **8**. In S_1 the excitation is largely localized on the CO group, and we find expulsion of CO is the dominant if not the exclusive reaction mode. In S_2 the excitation is largely localized in the diene, and cyclobutene formation is observed. We had previously concluded[6] that cyclobutene formation from the singlet manifold occurs only from planar dienones such as **4**, **6** and **7**. In the case of **8**, it is conceivable that the S_2 state relaxes from a twisted (C_2) toward a planar (C_S) diene conformation, allowing disrotatory ring closure to compete efficiently with IC. We can examine this hypothesis through additional calculations on geometrically altered dienones. Furthermore, the similarity in the state diagram for **1a** and **8** suggests that the rate constants for ISC should be nearly identical for the two compounds. Differences in Φ_{ST} must therefore be attributable to structural effects on competitive reactions from S_1, in particular on the rate of decarbonylation. We are now determining these rate constants explicitly using fluorescence lifetime measurements.[29]

The striking similarities in the results of our theoretical calculations on **1a** and **8** suggest that wavelength dependent photochemistry should be observed for **1a** and probably other 3,5-cycloheptadienones and perhaps as a general feature of the photochemistry of β,γ-unsaturated ketones. We intend to explore this possibility.

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References and Notes

(1) Part XLIV of a series on the photochemistry of ketones in solution. Part XLIII: D. I. Schuster, G. C. Barile, and K. Liu, *J. Am. Chem. Soc.*, **97,** 4441 (1975).

(2) O. L. Chapman and G. W. Borden, *J. Org. Chem.*, **26,** 4185 (1961); O. L. Chapman, D. J. Pasto, G. W. Borden, and A. A. Griswold, *J. Am. Chem. Soc.*, **84,** 1220 (1962).

(3) D. I. Schuster, B. R. Sckolnick, and F.-T. H. Lee, *J. Am. Chem. Soc.*, **90,** 1300 (1968); D. I. Schuster and D. J. Blythin, *J. Org. Chem.*, **35,** 3190 (1970).

(4) K. N. Houk, private communications; we are grateful to Professor Houk for sending us a copy of a comprehensive review on the photochemistry of β,γ-unsaturated carbonyl compounds prior to publication.

(5) For a review of this reaction, also known as the oxa-di-π-methane rearrangement, see S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, *Chem. Rev.*, **73,** 531 (1973).

(6) D. I. Schuster and C. W. Kim, *J. Am. Chem. Soc.*, **96,** 7437 (1974).

(7) K. Kurabayashi and T. Mukai, *Tetrahedron Lett.*, 1049 (1972); L. A. Paquette, R. H. Meisinger, and R. E. Wingard, Jr., *J. Am. Chem. Soc.*, **94,** 2155 (1972); T. A. Antkowiak, D. C. Sanders, G. B. Trimitsis, J. B. Press, and H. Shechter, *ibid.*, **94,** 5366 (1972).

(8) T. Mukai, Y. Akasaki, and T. Hagiwara, *J. Am. Chem. Soc.*, **94,** 675 (1972).

(9) K. N. Houk and D. J. Northington, *J. Am. Chem. Soc.*, **94,** 1387 (1972).

(10) L. A. Paquette, R. F. Eizember, and O. Cox, *J. Am. Chem. Soc.*, **90,** 5153 (1968).

(11) Spectral properties of **10:** NMR δ_{TMS} (CCl_4) 1.76 (br s, 12 H, methyls), 5.6–6.3 (complex m, 4 H, vinyls); uv λ_{max} (CH_3OH) 292 (ϵ 38,600), 280 (ϵ 55,000), 269 nm (ϵ 38,600); ir ν (CCl_4) 3040, 2970, 2920, 2860, 1640, 1380, 1000, 960 cm^{-1}, no ν_{CO}.

(12) R. M. Coates and W. H. Robinson, *J. Am. Chem. Soc.*, **94,** 5920 (1972); we are grateful to Professor Coates for sending us spectra of **10.**

(13) D. M. Burness, "Organic Syntheses," Coll. Vol. V, Wiley, New York, N.Y., 1973, p 403; K. Alder, H. Betzing, and K. Heimbach, *Justus Liebigs Ann. Chem.*, **638,** 187 (1960).

(14) G. Wittig and D. Wittenberg, *Justus Liebigs Ann. Chem.*, **606,** 1 (1957).

(15) E. F. Ullman and P. Singh, *J. Am. Chem. Soc.*, **94,** 5077 (1972).

(16) Spectral properties of **12:** NMR δ_{TMS} (CCl_4) 1.02 (s, 6 H, methyls), 1.10 (s, 6 H, methyls), 3.16 (s, 2 H, methynes), 6.25 (s, 2 H, vinyls); ν_{CO} 1725 cm^{-1}.

(17) Spectral properties of **13:** NMR δ_{TMS} (CCl_4) 1.07 (s, 6 H, methyls), 1.75 (br s, 6 H, methyls), 3.70 (br d, 1 H, αH), 4.80 (br d, 1 H, exocyclic vinyl), 5.92 (br s, 2 H, vinyls); ν_{CO} 1740 cm^{-1}.

(18) J. A. Pople and D. Beveridge, "Approximate Molecular Orbital Theory", McGraw-Mill, New York, N.Y., 1970.

(19) The one-center electron repulsion integrals γ_{AA} were taken from ref 20a and the $\beta_A{}^\circ$ parameters were taken from ref 20b. The π-overlap screening factors κ were chosen as $\kappa_{CC} = 0.570$ and $\kappa_{CO} = 0.750$, the optimal values found from calculations of transition energies in benzene and formaldehyde, respectively. Pariser's charged sphere approximation[21] was used forevaluating the two-center repulsion integrals γ_{AB}. The details of the present INDO model will be described elsewhere.[30]

(20) (a) J. Del Bene and H. H. Jaffé, *J. Chem. Phys.*, **48,** 1807, 4050 (1968); (b) R. L. Ellis, G. Kuehnlenz, and H. H. Jaffé, *Theor. Chim. Acta*, **26,** 131 (1972).

(21) R. Pariser and R. G. Parr, *J. Chem. Phys.*, **21,** 767 (1953).

(22) Interatomic Distances Supplement, *Chem. Soc.*, *Spec. Publ.*, **No. 18** (1965).

(23) See, e.g., R. G. Parr, "Quantum Theory of Molecular Electronic Structure," W. A. Benjamin, New York, N.Y., 1964.

(24) J. Linderberg and L. Seamans, *Int. J. Quantum Chem.*, **8,** 925 (1974).

(25) Calculated from the absorption spectrum by standard methods; see, e.g., N. Mataga and T. Kubota, "Molecular Interactions and Electronic Spectra", Marcel Dekker, New York, N.Y., 1970, p 212.

(26) J. Meinwald, S. L. Emerman, N. C. Yang, and G. Büchi, *J. Am. Chem. Soc.*, **77,** 4401 (1955); W. E. Parham, R. W. Soeder, J. R. Throckmorton, K. Kuncl, and R. M. Dodson, *J. Am. Chem. Soc.*, **87,** 321 (1965).

(27) N. J. Turro in "Energy Transfer and Organic Photochemistry", A. A. Lamola and N. J. Turro, Ed., Wiley-Interscience, New York, N.Y., 1972.

(28) K. N. Houk, D. J. Northington, and R. E. Duke, Jr., *J. Am. Chem. Soc.*, **94,** 6233 (1972).

(29) D. I. Schuster, J. Eriksen, P. S. Engel, and M. A. Schexnayder, paper to be submitted for publication.

(30) M. A. Ratner and K. Krogh-Jespersen, paper to be submitted for publication.

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Solvation of Gaseous Carbanions in Dimethyl Sulfoxide [1]

Sir:

We present here solvation energies for several classes of carbanions which are of importance to synthetic and theoretical organic chemistry. The effect of structural variation on their solvation energies can be understood roughly in terms of charge delocalization and steric hindrance to solvation.

Table I. Enthalpies of Deprotonation in the Gas Phase and DMSO for Protonic Acids with Corresponding Enthalpies of Solution of the Same Acids and Their Anions in DMSO[a]

No.	Compound	$\delta\Delta H_D$ DMSO	$\delta\Delta H_D{}^g$	$\delta\Delta H_S{}^{g\text{-DMSO}}$	$\delta\Delta H_S{}^{g\text{-DMSO}}(A^-)$[g]
1	Cyclopentadiene	0 (−24.44 ± 0.38)	0 (352.7)[b]	0 (−6.15 ± 0.06)	0 (−69.69)
2	1,4-Pentadiene	16.41 ± 0.39	7.0[b]	0.37[f]	9.78
3	Diphenylmethane	17.88 ± 0.42	7.9[b]	0.23[f]	10.21
4	Fluorene	6.24 ± 0.55	−4.2[b]	−0.15[f]	10.29
5	Acetonitrile	17.05 ± 0.39	8.8[b]	−2.16	6.09
6	Phenylacetonitrile	5.36 ± 0.43	−4.0[b]	−1.68[f]	7.68
7	Malononitrile	−8.09 ± 0.48	−21.9[b]	0.45[f]	14.26
8	Acetone	9.39 ± 0.43	11.3[b]	−0.87	−2.83
9	Acetophenone	7.09 ± 0.39	6.5[b]	−0.71[f]	−0.12
10	Phenylacetone	1.07 ± 0.43	−2.9[b]	−1.00[f]	2.97
11	Acetylacetone	−7.29 ± 0.51	−11.1[b]	−0.47[f]	3.34
12	Benzoylacetone	−8.49 ± 0.63	−14.9[b]	−0.48[f]	5.93
13	Dimedone	−9.49 ± 0.56	−18.6[b]	−1.51[f]	7.60
14	Phenol	0.14 ± 0.55	−5.8[b]	−5.47[f]	0.47
15	*tert*-Butylacetylene	18.42 ± 0.38	14.7[c]	−2.8[f]	3.44
16	Methanol[e]	8.44 ± 0.48	24.1	−3.1 ± 0.08	−18.76
17	Ethanol[e]	13.34 ± 0.55	22.2	−3.67 ± 0.07	−12.53
18	Isopropyl alcohol[e]	14.94 ± 0.43	20.8	−3.79 ± 0.07	−9.65
19	*tert*-Butyl alcohol[e]	15.24 ± 0.55	20.0	−3.01 ± 0.1	−7.77
20	Neopentyl alcohol[e]	13.84 ± 0.55	18.7	−4.35 ± 0.3	−9.21
21	Di-*tert*-Butylcarbinol[e]	16.94 ± 0.48	17.0	−6.02 ± 0.2	−6.08
22	Water[e]	12.24 ± 0.43	37.3	−5.64 ± 0.06	−30.70
23	Hydrogen chloride	−10.56 ± 1.07	−19.7[d]	−11.22 ± 0.3	−2.08
24	Hydrogen bromide	−9.54 ± 1.16	−29.7[d]	−17.97 ± 0.4	2.19
25	Hydrogen iodide	−16.58 ± 1.16	−39.7[d]	−19.10 ± 0.9	4.02

[a] All values relative to cyclopentadiene. [b] From ref 5. [c] From R. T. McIver, Jr., and J. S. Miller, *J. Am. Chem. Soc.*, 96, 4323 (1974). [d] From J. L. Beauchamp, *Annu. Rev. Phys. Chem.*, 22, 527 (1971). [e] From ref 4. [f] Estimated, see text. [g] See ref 4 for method of calculation.

The Brönsted acidity of carbon, oxygen, nitrogen, and sulfur acids has long been a subject of curiosity to physical organic chemists.[2] The crucial observation by Brauman and Blair[3] that "inherent" gas phase acidities can be exactly the reverse of those in solution has focused attention on the commanding role which anion solvation may play in determining relative acidities. In collaboration with McIver, we reported recently on the solvation enthalpies of seven alkoxyanions into dimethyl sulfoxide (DMSO).[4] Since then Kebarle's group[5] has reported gas phase acidities for a number of ketones, nitriles, and conjugated polyolefins. Bordwell[6] has shown parallel trends between Kebarle's results in the gas phase and pK_a's for the same acids in DMSO. We have reported previously[7a] a close correlation between pK_a's in DMSO and the corresponding heats of deprotonation, ΔH_D, for many types of Brönsted acids in that solvent.[8] In view of the crucial role of carbanions in synthetic chemistry[9] and the dramatic effects which may result from anion solvation[2c,3,4] we wish to report experimental solvation enthalpies of the anions $\Delta H_S{}^{g\text{-DMSO}}$ (A^-) derived from carbon, oxygen, and halogen acids presented in Table I. As before[4] gas phase heats of deprotonation, ΔH_D (g), were combined with heats of deprotonation in DMSO, ΔH_D (DMSO) (using the potassium lyate salt (K^+DMSYL^-) as base), through estimated (see below) heats of solution of the neutral acids into DMSO.[10] In contrast to our previous report, we have normalized all thermodynamic properties relative to cyclopentadienyl—rather than to *tert*-butoxy—anion. Actual values for each acid and its anion can be determined by adding the value shown in parentheses below cyclopentadiene to the relative property: the relative heat of deprotonation in the gas phase, $\delta\Delta H_D$ (g); the relative heat of deprotonation in DMSO, $\delta\Delta H_D$ (DMSO); the relative heat of solution of the neutral acid from the gas phase to DMSO, $\delta\Delta H_S{}^{g\text{-DMSO}}$ (AH); and the relative heat of solvation of the ion from the gas phase to DMSO, $\delta\Delta H_S{}^{g\text{-DMSO}}$ (A^-).

$\Delta H_S{}^{g\text{-DMSO}}$ (AH) normally would be calculated from the heat of vaporization or sublimation of AH and the heat of solution of liquid or solid AH in DMSO. Unfortunately, the necessary vaporization data for many of the compounds in Table I are not available. Worse still, the published values for some of the others disagree so badly (in some cases by over 6 kcal/mol) that we were unable to use them. Fortunately, it is not really the heats of vaporization which are needed for comparison of solvation enthalpies but the *differences* between the heats of solution for the various compounds into DMSO from the gas phase. In order to estimate the *relative* order for $\delta\Delta H_S{}^{g\text{-DMSO}}$ (AH) we used the assumption, based on our previous experience, that such differences will normally be small and proportional to the heat of transfer from an "inert" solvent to DMSO. This assumption was tested with methanol, ethanol, acetonitrile, cyclopentadiene, and acetone, compounds whose heats of vaporization we believe to be reliable.

In Figure 1, $\delta\Delta H_D$ (g) are plotted against corresponding relative solvation enthalpies $\delta\Delta H_S{}^{g\text{-DMSO}}$ (A^-). The former property represents the comparative energy of proton transfer from each acid to cyclopentadienyl anion and presumably is governed mainly by the inherent stabilities of the anions. $\delta\Delta H_S{}^{g\text{-DMSO}}$ (A^-) is the difference between the energy that is gained by interaction of the ion with the solvent—chiefly through ion-dipole and dispersion force interactions—and the energy required to produce a cavity in the solvent at the expense of solvent-solvent interactions.[11]

Figure 1 may be interpreted readily in terms of the interplay between anion stabilization by internal charge delocalization and by solvation. The results are differentiated clearly into four correlation lines representing different functional groups, the intersections being especially intriguing.

The slopes of the three nearly parallel lines for sterically unencumbered anions show a common inverse relationship between ionic size and solvation energy. However, other factors are also clearly at work. On the top line, showing the lowest solvation enthalpies, are the conjugate bases of hydrocarbons and nitriles presumably reflecting the highest degree of internal anion stability[12] and hence the least ten-

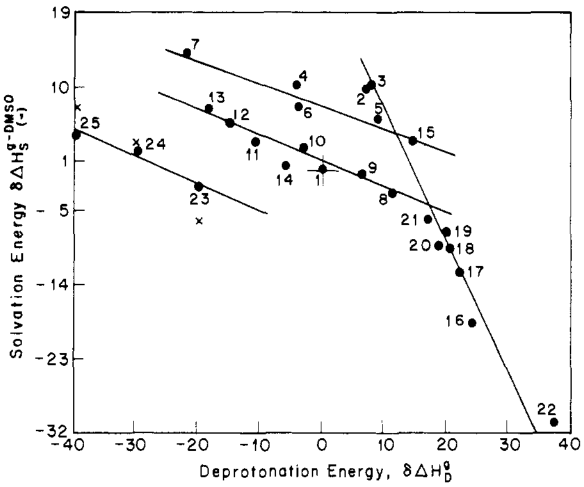
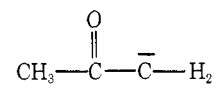


Figure 1. Comparison of gas phase deprotonation enthalpies of protonic acids in Table I, relative to cyclopentadiene, with corresponding solvation enthalpies of their anions in DMSO. Values for halide ions in water (X) estimated from enthalpies of transfer in ref 13.

dency toward solvation by ion–dipole interactions at a specific site. The differentiated solvation energies of $N{\equiv}C{-}CH_2^-$, $t\text{-}Bu{-}C{\equiv}C^-$, and


$CH_3-\overset{O}{\overset{\|}{C}}-\overset{-}{C}-H_2$

are interesting in view of the nearly equal gas phase acidities of their neutrals. The position of the acetonyl anion is especially noteworthy since it links the charge-delocalized enolates with charge-localized alkoxides.

The spherical halide ions, unencumbered with organic groups, provide the normative electrostatic model for the effect of ion solvation. The difference between their behavior in aprotic DMSO and in water[13] is attributed to differences in polarizability and hydrogen bonding. The unusually high solvation enthalpy of cyclopentadienyl anion relative to the other hydrocarbanions is consistent with Bordwell's proposal that dispersion force solvation is important here because of its unique degree of symmetrical charge delocalization over a relatively small volume.

Finally, we emphasize the striking sensitivity of alkoxide ion solvation energies to elaboration of the alkyl group. When contrasted with the other organic ions, their behavior strongly confirms our previous suggestion[4] that steric hindrance to ion solvation is responsible for the dramatic difference between their basicity in the gas phase and that in solution. The possibilities for exploiting this phenomenon have already been noted.[14]

On the recommendation of a referee we wish to point out that the *accuracy* of some of the gas phase data, on which the derived solvation enthalpies depend, is questionable since they have not all been linked together by stepwise equilibration. We have therefore not reported the standard deviations of solvation enthalpies in the last column of Table I since such formal estimates of *precision* could give a misleading impression of their ultimate reliability. However, we have confidence in the basic conclusions expressed here for the following reasons: (a) Taft[15] has found close agreement between Kebarle's high pressure mass spectrometry results and independent icr equilibration studies, (b) the alkoxide values were in fact based on gas phase equilibration,[4] (c) Bordwell[6] has noted systematic agreement between Kebarle's gas phase acidities and pK_a's in DMSO for series of similar carbon acids. His results, like those in Figure 1, suggest that major inaccuracies in the gas phase acidities would probably result in vertical displacement of the parallel lines with respect to each other rather than their slopes.

Acknowledgments. We appreciate the kindness of Professors Kebarle and Bordwell for providing us with valuable unpublished data.

References and Notes

(1) This work was generously supported by N.S.F. Grant G.P. 6550-X.

(2) (a) M. Szwarc, "Ions and Ion Pairs on Organic Reactions", Vol. 2, Wiley, New York, N.Y., 1974; (b) "Carbanions, Living Polymers and Electron Transfer Processes", Wiley, New York, N.Y., 1968; (c) D. J. Cram, "Fundamentals of Carbanion Chemistry", Academic Press, New York, N.Y., 1965; (d) R. P. Bell, "The Proton in Chemistry", 2nd ed, Cornell University Press, Ithaca, N.Y., 1973; (e) A. Streitwieser, Jr., *Prog. Phys. Org. Chem.*, **3,** (1965); (f) O. A. Reutov, K. P. Butin, and I. P. Beletskaya, *Russ. Chem. Rev.*, 43(1) (1974); (g) J. R. Jones, "Ionization of Carbon Acids", Academic Press, New York, N.Y., 1973.

(3) J. I. Brauman and L. K. Blair, *J. Am. Chem. Soc.*, **90,** 6561 (1968).

(4) E. M. Arnett, L. E. Small, R. T. McIver, Jr., and J. S. Miller, *J. Am. Chem. Soc.*, **96,** 5638 (1974).

(5) T. B. McMahon and P. Kebarle, *J. Am. Chem. Soc.*, **96,** 5940 (1974).

(6) F. G. Bordwell, J. E. Bartmess, G. E. Drucker, Z. Margolin, and W. S. Matthews, *J. Am. Chem. Soc.*, **97,** 3226 (1975).

(7) (a) E. M. Arnett, T. C. Moriarity, L. E. Small, J. P. Rudolph, and R. P. Quirk, *J. Am. Chem. Soc.*, **95,** 1492 (1973); (b) E. M. Arnett and T. C. Moriarity, *ibid.*, **93,** 4908 (1971).

(8) Extensive subsequent research in collaboration with Bordwell's group confirms and improves the original correlation. Our joint efforts will be presented in detail in a full report.

(9) H. O. House, "Modern Synthetic Reactions", W. A. Benjamin, Menlo Park, Calif., 1972.

(10) Corresponding free energies and entropies of solvation would be interesting but the necessary Henry's law constants for these compounds over DMSO are not available. In view of the remarkably good correlation of our ΔH_D (DMSO) values with Bordwell's pK_a's[7a,8] we doubt if relative free energies of solvation in DMSO for this series will differ drastically from their relative heats of solvation.

(11) Evidence that ion-pairing energies between these anions and the potassium counterion are negligible is found in (a) the close correlation of our data with Bordwell's[7a,8] although his anion concentration is a hundredfold[7a] less than ours and (b) the insensitivity of our ΔH_D (DMSO) values for acetylacetone, phenylacetonitrile, and cyclopentadiene to the addition of di-benzo-18-crown-6 ether—a strong complexing agent for potassium ion.[7b]

(12) J. Chaudhuri, J. Jagur-Grodzinski, and M. Szwarc, *J. Phys. Chem.*, **71,** 3063 (1967), have previously noted a close correlation between the electron affinities of polycyclic aromatic hydrocarbons in THF and in the gas phase.

(13) B. G. Cox, *Annu. Rep. Prog. Chem.*, **70,** (Section A) (1973).

(14) (a) C. A. Brown, *J. Org. Chem.*, **39,** 1324 (1974); (b) *Ibid.*, **39,** 3913 (1974); (c) *J. Am. Chem. Soc.*, **95,** 982 (1973).

(15) R. W. Taft in "Proton Transfer Reactions", Chapman and Hall, London, 1975.

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Transition Metal Catalyzed Acetylene Cyclizations. 4,5-Bis(trimethylsilyl)benzocyclobutene, a Highly Strained, Versatile Synthetic Intermediate

Sir:

Benzocyclobutenes, valuable precursors to theoretically interesting molecules,[1] are now gaining increasing importance as intermediates toward the synthesis of natural products.[2,3] For this purpose complete control of substitution in the aromatic ring of benzocyclobutene is highly desirable and has been the source of considerable synthetic difficulty.[4] We have recently developed a general synthesis of benzocyclobutenes via the cooligomerization[5] of 1,5-hexadiynes and substituted acetylenes using a cobalt catalyst.[6] Yields, however, were only moderate (ca. 15%) for functionalized systems, and benzocyclobutenes substituted by electrophilic moieties (halogen, acetyl, etc.) were inaccessible due to the instability of the corresponding acetylenic precursors and/or catalyst under the reaction conditions.[7]