recorded on a Thomas Hoover melting point apparatus and are corrected.

Diisopropylacetylene. A 1-L round-bottom flask was charged under argon with 14.2 g (0.1 mol) of 2,5-dimethylhex-3-yne-2,5-diol (Farchan) in 300 mL of dichloromethane. To the solution was added 34.5 g (0.1 mol) of dicobalt octacarbonyl (Strem) and the mixture was allowed to stir for 6 h. The flask was then cooled in an ice–salt water bath and 11.2 g (0.3 mol) of sodium borohydride powder was suspended in the reaction mixture, followed by the dropwise addition of 100 mL of trifluoroacetic acid over a period of 30–60 min. After 3 h the reaction was quenched by decanting the solution away from the residual sodium borohydride onto ice. The organic phase was separated and washed again with water. Without drying, demetallation was effected by adding approximately 150 g of $Fe(NO_3)_3 \cdot 9H_2O$ to the well-stirred solution in an oversized beaker. The solution was then again decanted away from the residue which was washed with a small portion (50 mL) of dichloromethane. The organic phase was dried over sodium sulfate. Fractional distillation of the dichloromethane solution left a dark liquid from which 7.8 g (70% yield) of diisopropylacetylene (bp 102–105 °C (lit.[4b] bp 104–106 °C)) was distilled. ^1H NMR ($CDCl_3$) δ 1.09 (d, 12 H, J = 6.8 Hz, $CH(CH_3)_2$), 2.48 (septet, 2 H, J = 6.9 Hz, $CH(CH_3)_2$) (lit.[6] δ 1.05, 2.35 (CH_2Cl_2)). ^{13}C NMR ($CDCl_3$) δ 20.5 ($CH(CH_3)_2$), 23.5 ($CH(CH_3)_2$), 85.0 (acetylene carbon).

The above procedure was repeated with 2,5-dimethylhex-3-yne-2,5-diol-d_{14},[43] trifluoroacetic acid-d_1, and $NaBD_4$ in place of the corresponding undeuterated reagents. The product, diisopropylacetylene-d_{14}, was characterized mass-spectrometrically and found to contain 97 atom % of deuterium.

Hexaisopropylbenzene. A 25-mL round-bottom flask was charged under argon with 5.0 g (45 mmol) of neat diisopropylacetylene and 0,5 g (1 mmol) of $Hg[Co(CO)_4]_2$[44] as catalyst. The flask was fitted with a reflux condenser and the mixture was heated under reflux overnight. A solid formed on cooling. The reaction mixture was dissolved in chloroform and chromatographed on silica (60–240 mesh), using hexane as eluent. The desired product was obtained as a white, crystalline solid, 1.6 g (31% yield), mp 285–287 °C (lit.[4a] mp 286 °C; lit.[4d] mp 286–286.5 °C). ^1H NMR ($CDCl_3$) δ 1.22 (d, 36 H, J = 7.2 Hz, $CH(CH_3)_2$), 3.68 (septet, 6 H, J = 7.2 Hz, $CH(CH_3)_2$) (lit.[4a,b] δ 1.27, 3.61 (CS_2)). ^{13}C NMR ($CDCl_3$) δ 22.9 (C_m), 27.6 (C_t), 144.7 (C_{ar}).

The above procedure was repeated with a mixture of diisopropylacetylene (0.5 g, 5 mmol) and diisopropylacetylene-d_{14} (7.0 g, 56 mmol), with 0.5 g of $Hg[Co(CO)_4]_2$. After chromatography on silica gel the isotopomer mixture was obtained as a white solid (2.3 g, 31%), mp 287–288° C, after recrystallization from pentane–ethanol.

Mass spectral peak heights were averaged over ten runs at 20 eV. Corrections were made for natural isotopic distribution in a hydrocarbon of formula $C_{24}H_{42}$. The adjusted data were then fit to Biemann's formula[45] and a percent distribution of isotopomers was obtained: d_{42} 82.6; d_{28} 15.8; d_{14} 1.3; d_0 ~0.

X-ray Crystallography. Crystals of **1** were obtained from a mixture of pentane and ethanol (3:1) by slow evaporation at −20 °C. A crystal of approximately 0.20 × 0.25 × 0.40 mm^3 was chosen for the X-ray measurements. Crystal data: $C_{24}H_{42}$, M_r = 330.34 g mol^{-1}; triclinic (space group $P\bar{1}$ assumed throughout); a = 6.400 (2) Å, b = 9.943 (3) Å, c = 10.223 (2) Å, α = 117.79 (2)°, β = 94.78 (3)°, γ = 105.58 (3)°, V = 536.7 Å^3; d_x = 1.022 g cm^{-3}, Z = 1. X-ray intensities were collected at 99 K on a four-circle diffractometer (CAD4) equipped with a nitrogen-flow cooling device applying Mo Kα radiation (λ = 0.71069 Å). A total of 3737 independent reflections were recorded with $\theta_{Mo} < 30°$ of which 2699 with $I > 3\sigma(I)$ were considered significant. The structure was solved by direct methods with MULTAN.[46] The carbon atoms were refined anisotropically, the hydrogens isotropically, by full-matrix least-squares with use of the 1964 significant reflections with $\sin \theta/\lambda >$ 0.45 Å^{-1}. Common population coefficients p and p' were refined for the methine carbons C_t and C_t' of the major and minor orientations, respectively, with the constraint $p + p' = 1$; the final value of p was 0.6748 (200). R and R_w factors after the refinement were 0.045 and 0.045, respectively.

Acknowledgments. We thank the National Science Foundation (CHE-8009670) for support of this work and Daniel Iverson and Robert Pascal for helpful discussions.

Registry No. 1, 800-12-4; 2,5-dimethylhex-3-yne-2,5-diol, 142-30-3; diisopropylacetylene, 927-99-1.

Supplementary Material Available: Final anisotropic thermal parameters for carbon atoms, atomic coordinates of hydrogen atoms, and isotropic temperature factors, with standard deviations, for **1** (3 pages). Ordering information is given on any current masthead page.

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(43) This compound was prepared by reaction of acetylene and ethylmagnesium bromide, followed by addition of acetone-d_6 to the Grignard reagent and hydrolysis of the adduct with D_2O. Recrystallization from hexane gave a product (mp 89–91 °C) which was found by MS to contain 99 atom% of deuterium.

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Study of ^{13}C–^{13}C NMR Coupling Constants in α-Cyanodiarylmethyl and 1,1-Diaryl-2-butynyl Cations[1]

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Abstract: One-bond ^{13}C–^{13}C NMR coupling constants in α-cyanodiarylmethyl and 1,1-diaryl-2-butynyl cations were measured and compared to those in related neutral model compounds. The substituent effects on chemical shifts (SCS) and coupling constants (SCC) are discussed in light of charge delocalization into the neighboring cyano group or triple bond through contributing mesomeric nitrenium and allenyl cation structures. While $J_{C_i\text{–}C_\alpha}$ reflects the change in the bond order between C_i and C_α with respect to the nature of the substituent on the aryl ring, $J_{C_\alpha\text{–}C_\beta}$ is relatively insensitive to such changes.

It is well-known that one-bond ^{13}C–^{13}C coupling constants, $^1J_{CC}$, can be correlated to the percents character of the orbitals making up the bond.[2-4] Recently we reported[5] one-bond ^{13}C–^{13}C coupling constants in a series of acetophenones, benzaldehydes, and their O-protonated carboxonium ions using the INADEQUATE[6] pulse

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(1) Stable Carbocation. 266. For Part 265, see: de Meijere, A.; Schallner, O.; Goltiz, P.; Weber, W.; Schleyer, P. v. R.; Prakash, G. K. S.; Olah, G. A. *J. Org. Chem.* **1985**, *50*, 5255.

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Table I. ^{13}C NMR Chemical Shifts in 1,1-Diaryl-2-butynyl Cations, **4**[a]

R	C_1	C_2	C_3	C_4	C_α^+	C_β	C^γ	$CH_3(\delta)$	other
4-OCH_3[b]	132.9	142.4	117.0	172.1	175.0	85.0	138.6	6.7	57.0 (OCH_3)
4-CH_3[b]	137.8	140.6	131.9	159.9	187.9	89.3	153.0	8.1	22.5 (CH_3)
H[c]	144.8	141.5	131.4	145.4	195.7	93.2	165.1	9.1	

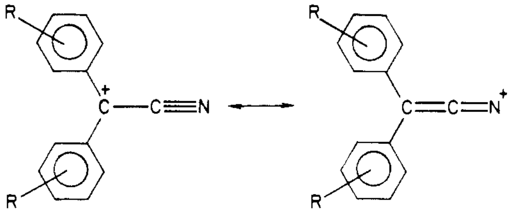
[a] ^{13}C chemical shifts are in ppm from external Me_4Si. [b] In FSO_3H/SO_2ClF at -85 °C. [c] In FSO_3H/SbF_5 (4:1)/SO_2ClF at -85 °C; ref 12.

sequence. It has been shown that increasing the double-bond character between the ipso and the carbonyl carbon by substitution on the aryl ring with electron-donating substituents increases the $J_{C_{ipso}-C_{carbonyl}}$ coupling constants. In other words, within a series of structurally similar compounds, one can use the magnitude of $^1J_{CC}$ values as a measure of the bond order between two carbon centers.

Solvolytic studies of Gassman andco-workers[7-9] have demonstrated the ambivalent nature of a α-cyano group on a carbocationic center. The cyano group being a strong electron-withdrawing group inductively destabilizes the carbocationic center. On the other hand, the major portion of this effect is offset by the stabilizing effect of the contributing mesomeric nitrenium ion structure **2**. Support for such a structure also comes from theoretical calculations.[10]

1 **2**

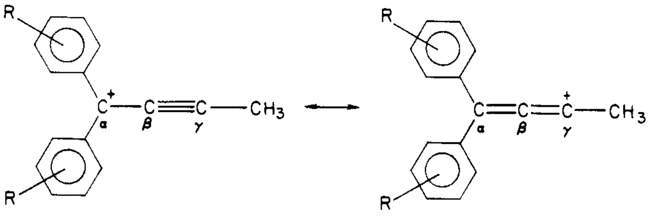
While bona fide nitrenium ions[11] have not been observed under stable ion condition, on the basis of ^{13}C, ^1H, and ^{15}N NMR spectroscopic studies, recently,[12] we have demonstrated that the stable, long-lived cyanodiarylmethyl cations, **3**, show significant mesomeric nitrenium ion character inspite of strong competitive aryl ring charge stabilization.



a **b**

3

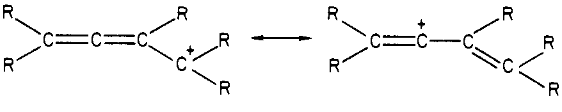
The structurally related, 1,1-diaryl-2-butynyl cations, **4**, are also of interest in that they show mesomeric vinylic cation character.



a **b**

4

So far, no vinyl cation has been observed under long-lived stable ion conditions. However, vinyl cation forms of propargylic cations (such as **4b**)[13,14] and allenyl carbinyl cations[15] (such as **5b**) have been shown to contribute quite heavily to the total ion structure.



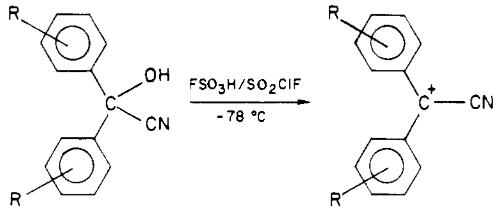
a **b**

5

It was consequently of substantial interest to study the effect of expected increased bond order between the cyano carbon and the cationic center in **3** and between C_α and C_β in **4** on the $^{13}C-^{13}C$ coupling constants between these centers. It was also of interest to compare the effect of substituents on the chemical shift and the J_{CC} values in these systems. We, therefore, undertook such a study and report herein our findings.

Results and Discussion

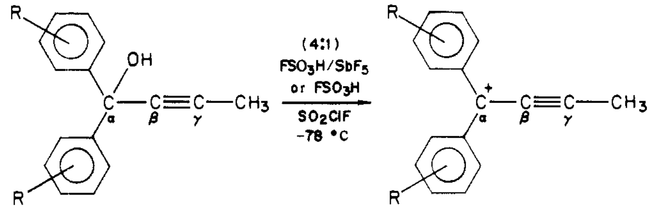
The substituted α-cyanodiarylmethyl cations, **3**, were prepared by the ionization of the corresponding cyanohydrins, **6**, in FSO_3H/SO_2 ClF at -78 °C. The ^{13}C and ^{15}N NMR data of the cyanodiarylmethyl cations have been reported earlier.[12]



6 **3**

(R = H, 4-CH_3, 4-OCH_3)

1,1-Diaryl-2-butynyl cations, **4**, were prepared by the ionization of the corresponding 1,1-diaryl-2-butyn-1-ols,[1,3b] in FSO_3H:SbF_5 (4:1) or FSO_3H in SO_2ClF at -78 °C. The ^{13}C NMR chemical shifts are listed in Table I.



7 **4**

(R = H, 4-CH_3, 4-OCH_3)

All attempts to observe $^{13}C-^{13}C$ satellites of these ions in natural-abundance ^{13}C NMR spectra using the INADEQUATE pulse sequence were unsuccessful. The extremely slow relaxation rates of both the cationic carbon and the cyano (in **3**)/C_β (in **4**) carbon compounded with the low concentration of the ion in the superacidic media make it extremely difficult to observe the

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Table II. J_{CC} Values in α-Cyanocarbenium Ions, **3**, 1,1-Diaryl-2-butynyl Cation, **4**, and Other Representative Model Compounds

compd/ions	$^1J_{CC}{}^a$, Hz	compd/ion	$J_{CC}{}^a$
6-H	J_{C_i},C(OH) = 49.3 $J_{C(OH),CN}$ = 63.7	**7**-H	$J_{Ci,C\alpha}$ = 49.4 J_{C_α,C_β} = 79.2
6-CH_3	$J_{C_i,C(OH)}$ = 50.1 $J_{C(OH),CN}$ = 63.5	**7**-CH_3	J_{Ci,C_α} = 49.2 J_{C_α,C_β} = 79.2
6-OCH_3	$J_{C_i,C(OH)}$ = 51.4 $J_{C(OH),CN}$ = 62.9	**7**-OCH_3	$J_{Ci,C\alpha}$ = 51.1 $J_{C_\alpha,C\beta}$ = 78.4
3-H	J_{C_i,C^+} = 59.3[b] $J_{C^+,CN}$ = 75.5[b]	**4**-H	$J_{C_i,C\alpha}$ = 54.0[c] J_{C_α,C_β} = 90.5[c]
3-CH_3	J_{Ci,C^+} = 61.2[b] $J_{C^+,CN}$ = 76.4[b]	**4**-CH_3	J_{C_i,C_α} = 55.9[b] J_{C_α,C_β} = 90.2[b]
3-OCH_3	J_{C_i,C^+} = 64.0b $J_{C^+,CN}$ = 77.5[b]	**4**-OCH_3	J_{C_i,C_α} = 58.4[b] J_{C_α,C_β} = 90.2b
C_6H_5—C_αH═C_βH—CN (trans)	$J_{C_i-C_\alpha}$ = 55.7 $J_{C_\beta,CN}$ = 81.5 J_{C_α,C_β} = 73.9	$(C_6H_5)_2$CH—CN	$J_{C(H),CN}$ = 58.2
4-CH_3—C_6H_4—C_αH═C_βH—CN (trans)	J_{C_i},C_α = 56.5 $J_{C_\beta,CN}$ = 81.5 J_{C_α,C_β} = 73.7	C_6H_5—CN	$J_{C_i,CN}$ = 80.8
4-CH_3O—C_6H_4—C_αH═C_βH—CN (2 isomers)	J_{C_i,C_α} = 57.4; 57.2 $J_{C_\beta,CN}$ = 81.5; 77.9 J_{C_α,C_β} = 74.0; 73.8	C_6H_5—C_α≡C_βH	J_{Ci,C_α} = 89.0

[a] All coupling constants are in hertz; the value for the neutral compounds are ±0.2 Hz in $CDCl_3$ at 20 °C. [b] ±1 Hz in FSO_3H/SO_2ClF at −85 °C. [c] ±1 Hz in FSO_3/SbF_5 (1:4)/SO_2ClF at −85 °C.

satellite peaks in accessible instrument time. Thus, in order to increase the intensity of the satellite signals, we prepared the cyanohydrins, **6**, with ~45% ^{13}C enrichment on the cyanohydrin carbon and the propargyl alcohols, **7**, with ~45% ^{13}C enrichment at the C_α carbon. The enriched cyanohydrins were prepared from the corresponding ^{13}C-enriched substituted benzophenones[16] (with ^{13}C enrichment on the carbonyl carbons) and trimethylsilyl cyanide.[17] The enriched propargyl alcohols were prepared by reacting 1-propynyllithium with ^{13}C-enriched substituted benzophenones. Ionization of enriched precursors gave **3** with ^{13}C enrichment on the cationic carbon and **4** with ^{13}C enrichment on the C_α carbon. The cyano carbon and ipso carbon in **3** and the ipso and C_β carbons in **4** appear as pseudotriplets, and the coupling constants can be directly measured from the proton-noise-decoupled ^{13}C spectra. The ^{13}C–^{13}C coupling constants measured in the present study are listed in Table II. In order to reconfirm the coupling constant values in **3** (measured from the ion with ^{13}C enrichment at the cationic carbon), we also prepared and ionized the cyanohydrins, **6**, with ~45% ^{13}C enrichment on the cyano carbon prepared from the corresponding benzophenones and ^{13}C-enriched trimethylsilyl cyanide. The coupling constants measured from such ions correspond well with those obtained from ions with ^{13}C enrichment at the cationic carbon.

Table II also lists $J_{C_i-C(OH)}$ and $J_{C(OH)-CN}$ in the cyanohydrins, **6**, and $J_{C_i-C_\alpha}$ and $J_{C_\alpha-C_\beta}$ in the propargyl alcohols, **7**. These values were measured from the ^{13}C spectrum of the corresponding ~45% ^{13}C-enriched compounds. One-bond ^{13}C–^{13}C coupling constants values of some representative model neutral compounds are also listed in Table II. These were measured at natural abundance by using the INADEQUATE pulse sequence.

Substituent Effect on Chemical Shifts. The effects of substituents on the ^{13}C and ^{15}N NMR chemical shifts in α-cyanodiarylmethyl cations, **3**, have been analyzed earlier[12] which supports the charge delocalizing ability of the α-cyano group through a mesomeric nitrenium ion structure. The major evidence comes from the ^{15}N chemical shift shielding effect that is observed with an increase in the electron-donating ability of the substituent.

In the case of propargyl cations (Table I), **4**, both the C_α and C_γ chemical shifts are shielded with electron-donating substituents indicative of a decreased contribution by the contributing allenyl resonance structure, **4b**, with an increase in the charge delocalization into the aryl groups. The C_β chemical shift is also shielded with electron-donating substituents, although the effect is much less significant compared to C_α and C_γ. The similarity in the substituent effects observed in the C_α and C_γ chemical shifts in **4** and the cationic carbon and cyano nitrogen chemical shifts in **3**[12] is a clear indication of the similar behavior of these two related systems.

^{13}C–^{13}C Coupling Constants. Three types of interactions seem to dominate the coupling between nuclear spins via electrons according to Ramsey's theory.[18] (i) Fermi contact between the nuclear moments and electronic spins predominantly in the σ orbitals, (ii) orbital interaction between the nuclear moments and electronic currents produced by the orbiting electrons, and (iii) dipole interactions between nuclear and electronic moments. These contributions may vary in sign as well as in magnitude. For the majority of the first-row elements, the coupling is dominated by the Fermi contact term.[19-25] Thus, coupling constants can be correlated to the percents character of the orbitals making up the bond. In unsaturated systems containing π bonds, the noncontact contributions can also become important. From the work of Maciel et al.,2[6] it is recognized that neither simple hybridization theory nor effective nuclear charge densities are adequate enough to account for the observed trends of J_{CC} values in simple homologous series of compounds.

In our recent study,[5] we analyzed $J_{C_{ipso}-C_{carbonyl}}$ in substituted acetophenones, benzaldehydes, and their O-protonated carboxonium ions, in terms of resonance, inductive, and electronegativity effects of the substituents. We were able to show that the changes in the C_{ipso}–$C_{carbonyl}$ coupling constant qualitatively reflect the change in the double-bond character between the C_{ipso}–$C_{carbonyl}$ bond. This was found in agreement with the conclusions of Contreras et al.,[27]

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(16) ^{13}C-enriched substituted benzophenones were prepared from ^{13}C-enriched substituted benzoic acids by the following reaction sequence:

$$R\text{-}C_6H_4{}^*COOH \xrightarrow[Et_2O]{SOCl_2/} R\text{-}C_6H_4{}^*COCl \xrightarrow[AlCl_3]{C_6H_5\text{-}R} R\text{-}C_6H_4\text{-}{}^*CO\text{-}C_6H_4\text{-}R$$

where R = H, p-CH_3, and p-OCH_3.

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who calculated the σ- and π-transmitted components of Fermi contact, spin-dipolar, and orbital terms of one-bond and long-range C–C coupling constants in several unsaturated hydrocarbons using the SCPT-INDO method. Their studies showed that although the σ components of all three terms are far more important, the contribution of the π component is also significant, particularly in the substituent effect on ^{13}C–^{13}C coupling constants (SCC). Although theoretical studies are important, it is also essential to obtain experimental J_{CC} values[28,29] in representative systems to establish empirical correlations with other molecular properties which are dependent on the same electronic characteristics of the molecules.

The J_{C^+-CN} values in α-cyanodiarylmethyl cations, **3** are in the order of 76.5 ± 1 Hz. These values are similar to the J_{Ci-CN} values in benzonitriles and $J_{C_\beta-CN}$ values in cinnamonitriles (ref. Table II). This could be taken as evidence for a comparable bond between the carbocationic center center and the cyano carbon and those between C_{ipso} and CN in benzonitriles and C_β and CN in cinnamonitriles. The $^1J_{C^+-CN}$ values (75.5 Hz) in the α-cyanodiphenylmethyl cation (**3**, R = H) are 11.9 Hz higher than the corresponding value (63.6 Hz) in the precursor benzophenone cyanohydrin (**6**, R = H) and 17.3 Hz higher than that (58.2 Hz) in diphenylacetonitrile. Similar large differences are observed in the J_{C^+-CN} values between the α-cyanodi-*p*-tolylmethyl cation (**3**, R = 4-CH_3; $^1J_{C^+-CN}$ = 76.4 Hz) and 4,4′-dimethylbenzophenone cyanohydrin (**6**, R = 4-CH_3; $^1J_{C-CN}$ = 63.6 Hz) and between the α-cyanodi-*p*-anisylmethyl cation (**3**, R = 4-OCH_3; $^1J_{C^+-CN}$ = 77.5 Hz) and 4,4′-dimethoxybenzophenone cyanohydrin (**6**, R = 4-OCH_3; J_{C-CN} = 63.0 Hz). Such a large difference between $J_{C_\alpha-C^+}$ in a cation and the $J_{C_\alpha-C(OH)}$ in the corresponding alcohol or the $J_{C_\alpha-C(H)}$ in the corresponding hydrocarbon is unusual. For example, $J_{C_1-C_2}$ in adamantane is 31.6 Hz,[30] and the $J_{C_\alpha-C^+}$ in the 1-adamantyl cation is 31.2 Hz.[31] Similarly J_{CC} in isobutane is 34,7 Hz,[31] and the $J_{C_\alpha-C^+}$ in the *tert*-butyl cation is 30.5 Hz,[31,32] whereas, the J_{Ci-C^+} in the cumyl cation (51.6 Hz)[31] is much higher than the J_{Ci-CH} in cumene (43,3 Hz),[31] apparently reflecting increased double-bond character between the C_i and C^+ in the former due to aryl ring charge delocalization. In view of these, the substantial difference (17.3 Hz) in J_{C-CN} between diphenylacetonitrile and the cyanodiphenylmethyl cation may be interpreted as due to the substantial increase in the bond order between the cyano carbon and the cationic center because of charge delocalization by the cyano group through the mesomeric nitrenium ion structure, **3b**, although such a conclusion may be speculative.

The $J_{C_\alpha-C_\beta}$ values in 1,1-diphenyl-, 1,1-di-*p*-tolyl-, and 1,1-di-*p*-anisyl-2-butnyl cations, **4**, are 90,5, 90.2, and 90.2 Hz, respectively. The $J_{C_\alpha-C_\beta}$ values in these cations are ∼11 Hz higher than those in the corresponding alcohols, **7**. Such a large difference between the cations and the precursor alcohols may, again, be interpreted as due to the contribution of the allenyl resonance structure, **4b**. A comparison of the $J_{C_\alpha-C_\beta}$ values in the propargyl cations, **4**, with the J_{C^+-CN} values in the α-cyanocarbenium ions, **3**, shows a difference of ∼13 Hz, However, the $J_{Ci-C\alpha}$ in phenylacetylene (89.0 Hz) and the J_{Ci-CN} in benzonitrile (80.8 Hz) differ by ∼8 Hz. Consequently, the difference of ∼13 Hz between J_{CC} values in **3** and **4** provides further evidence for the close similarity between the two systems.

The J_{C^+-CN} values in α-cyanodiarylmethyl cations, **3**, apparently remain a constant (within the experimental error of ±1 Hz) with respect to the nature of the substituent on the aryl ring. The previous analysis of the ^{13}C and ^{15}N chemical shift data[12] clearly indicates that the contribution of the mesomeric nitrenium ion structure **3b** decreases with an increase in the charge delocalization into the aryl rings by an electron-donating group. Thus, if J_{CC} was to reflect the change in the bond order between two carbon centers (as it does in the J_{Ci-CO} values in substituted acetophenones, benzaldehydes, and their O-protonated carboxonium ions[5]), one would expect the J_{C^+-CN} values to decrease with an increase in the electron-donating ability of the substituent. However, the observed values are practically insensitive to the nature of the substituents. On the other hand, the J_{Ci-C^+} values in **3** show the expected trend with respect to the nature of the substituent and are in the order *3*-OCH_3 (64.0 Hz) > *3*-CH_3 (61.2 Hz) > *3*-H (59.3 Hz). The change in the double-bond character between the C_i and C^+ with respect to the nature of the substituent is clearly reflected in these coupling constants.

An analysis of the J_{Ci-C_α} and $J_{C_\alpha-C_\beta}$ values in 1,1-diaryl-2-butynyl cations, **4**, also reveals the difference in the substituent effect on these coupling constants. The oserved J_{Ci-C_α} values in the 1,1-diaryl-2-butynyl cations show the expected trend with respect to the nature of the substituent and are in the order 4-OCH_3 (58.4 Hz) > 4-CH_3 (55.9 Hz) > 4-H (54.0 Hz). However, the $C_{\alpha-C\beta}$ coupling constant seems to be insensitive to the nature of the substituents and remains constant (≈90.0 Hz) throughout. Analysis of the chemical shifts in **4** shows that the contribution of the allenyl resonance structure, **4b**, decreases with the increased charge delocalization into the aryl ring. However, it is not reflected in the $J_{C_\alpha-C_\beta}$ values even though $J_{C_i-C_\alpha}$ does indeed show an increase in the aryl ring delocalization with increasingly electron-donating substituents.

A similar trend is observed in a series of cinnamonitriles. Whereas $J_{Ci-C\alpha}$ in the cinnamonitriles increases with the increased electron-donating ability of the substituent, $J_{C_\alpha-C_\beta}$ remains practically constant. This seems that in an aryl-substituted system with extended conjugation, while $J_{C_i-C_\alpha}$ qualitatively reflects the change in the bond order with respect to the nature of the substituent, $J_{C_\alpha-C_\beta}$ is relatively insensitive to such changes.

Conclusion

In summary, we measured J_{Ci-C^+} and J_{C^+-CN} in α-cyanodiarylmethyl cations, **3**, and J_{Ci-C_α} and $J_{C_\alpha-C_\beta}$ in 1,1-diaryl-2-butynyl cations, **4**. We also determined the corresponding values in their precursor alcohols. These values were compared with the corresponding values in substituted cinnamonitriles as the model compounds. Analysis of chemical shift of these ions indicates that there is a decrease in the contribution of the nitrenium ion structure in **3** and allenyl resonance structure in **4** with an increase in the electron-donating ability of the substituent on the aryl ring. However, the values of J_{C^+-CN} (in **3**) and $J_{C\alpha-C\beta}$ (in **4**) are practically insensitive to the nature of the substituent, while J_{Ci-C^+} in **3** and $J_{C_i-C_\alpha}$ in **4** increase with the electron-donating ability of the substituent. Similar observation is made in the corresponding J_{CC} values in substituted cinnamonitrile. Thus, in extended conjugated systems, while J_{Ci-C_α} reflects the change in the bond order between C_{ipso} and C_α with respect to the nature of the substituent, $J_{C_\alpha-C_\beta}$ remains relatively insensitive to these changes.

Experimental Section

All the cyanohydrins utilized in our study were prepared from the corresponding benzophenone and trimethylsilyl cyanide by using the procedure of Gassman and Talley.[17] The ∼45% ^{13}C-enriched trimethylsilyl cyanide was prepared[33] from enriched silver cyanide and trimethylsilyl chloride. The enriched silver cyanide was obtained by reacting aqueous silver nitrate solution with aqueous enriched sodium cyanide.

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[32] Our earlier reported (*J. Am. Chem. Soc.* **1974**, *96*, 2229) value of 25.1 Hz for J_{C^+,CH_3} in the *tert*-butyl cation is smaller than the value (30.5 Hz) obtained by using the INADEQUATE pulse sequence. This is due to the fact that the coupling constant measured earlier was obtained from the published spectrum where no complete peak separation to the base line was achieved. Indeed, the frequency of the separation of overlapping peaks will be less than the true coupling constant. This has been verified by line-shape analysis. The present value of 30.5 Hz is from peaks which are 180° phase-shifted and resolved to the base line.

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Preparation of Ions. Cyanocarbenium ions and propargyl cations were prepared from the progenitor cyanohydrins and propargyl alcohols as described earlier.[12,14]

The ^{13}C NMR spectroscopic studies were carried out at 50 MHz on a Varian XL-200 superconducting NMR spectrometer equipped with a variable-temperature broad-band probe. The ^{13}C–^{13}C coupling constants in the ^{13}C-enriched ions and the progenitors were directly measured from their proton-noise-decoupled ^{13}C NMR spectra. The coupling constants in the other neutral model compounds reported in Table II were measured from the ^{13}C satellite spectra by using the INADEQUATE[6] pulse sequence: $90°\ (x)-\ \tau-180°\ (\pm y)-\ \tau-90°\ (x)-\ \Delta-90°\ (\phi)\simeq$Acq. (ψ), where $\tau \simeq (2n + 1)/4J_{CC}$, Δ is a very short delay ($\sim$10 μs) needed to reset the radiofrequency phase during which time double-quantum coherance evolves and ϕ and ψ are the phase of the last 90° "read" pulse and the receiver, respectively.

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Essentially Solvent-Independent Rates of Solvolysis of the 1-Adamantyldimethylsulfonium Ion. Implications Regarding Nucleophilic Assistance in Solvolyses of *tert*-Butyl Derivatives and the N_{KL} Solvent Nucleophilicity Scale[1]

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Abstract: Rearside nucleophilic solvation of the developing carbocation is severely hindered during the solvolysis of the 1-adamantyldimethylsulfonium ion (1-AdSMe$_2^+$). For variation in the composition of binary solvent systems, the ion always shows a variation of the specific rate in the opposite direction to that observed for the *tert*-butyldimethylsulfonium ion (*t*-BuSMe$_2^+$); these observations are rationalized in terms of a dominant nucleophilic solvation at the transition state for *t*-BuSMe$_2^+$ solvolysis and a dominant nucleophilic stabilization of the reactant for 1-AdSMe$_2^+$ solvolysis. These systems are compared to the corresponding alkyl halides. Corrections applied in setting up the N_{KL} scale of solvent nucleophilicities would be better based on 1-AdSMe$_2^+$ solvolyses. However, the insensitivity of 1-AdSMe$_2^+$ solvolyses to solvent variation (specific rates in 41 solvents, at 70.4 °C, vary by less than a factor of seven) allows $\log (k/k_0)_{Et_3O^+}$ values to be taken as a good measure of solvent nucleophilicity. For solvolyses of 1-AdSMe$_2^+$ in aqueous ethanol ($\geq$60% ethanol), the S value (favoring reaction with water) is 1.35 at both 70.6 and 100.1 °C.

Considerable interest centers around the extent to which specific rates of solvolysis of *tert*-butyl chloride are influenced by the nucleophilicity of the solvent. Evidence for[2-10] and against[11-16] detectable interaction of the solvent has been presented. The original Grunwald–Winstein equation[17] (eq 1) defines a scale of

$$\log (k/k_0) = mY \qquad (1)$$

solvent ionizing power (Y) in terms of the specific solvolysis rates of *tert*-butyl chloride in a given solvent (k) and in 80% ethanol (k_0), with m assigned a value of unity. Accordingly, the detailed mechanism has important implications both as regards the significance of the Y scale and as regards the types of substrates for which it can logically be used in correlation analysis.

In a discussion of solvation effects upon S_N1 and E1 reactions, Ingold stated[18] "in the unimolecular substitution of an alkyl halide, both of the ions, which are formed in the initial heterolysis, have to be solvated". While the nucleophilic solvation of a developing bridgehead carbocation will necessarily be relatively weak, appreciable rearside solvation is possible for a developing *tert*-butyl carbocation.[19,20] In accord with the description of Ingold, we have considered[8] the solvolysis of *tert*-butyl chloride to involve carbenium ion formation, with the need to consider solvation of *both* of the incipient ions. Bentley and co-workers[7,9] have viewed the mechanism in a slightly different way and have formulated it as an example of an S_N2 (intermediate) mechanism.[21] Other workers[13-16] have, however, proposed that changes in the specific solvolysis rate, accompanying changes in the solvent, can be rationalized without the need to consider the nucleophilicity of the solvents.

If our view of the solvation process[8,18] is accepted, the original Y scale[17] is valid as a scale of solvent ionizing power. However, it should be used within eq 1 only for the correlation of solvolyses within which a similar (relatively small) contribution from nu-

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