

Coordination, Heterolysis, and Electron-Transfer Reactions Involving Delocalized Carbocations and Carbanions in Solution

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Contribution from the Department of Chemistry, Duke University, Durham, North Carolina 27706. Received January 30, 1984.
Revised Manuscript Received May 17, 1984

Abstract: The effect of structure and reaction conditions on carbon-carbon bond formation was investigated by the direct reaction of resonance-stabilized carbocations and carbanions in solution. Preliminary results indicated rates of coordination that range from diffusion controlled for the least stable ions to a total lack of reaction for the most stable ones after months of standing at room temperature. These results suggested that coordination/heterolysis equilibria could be established for reversible reactions of carbocations with carbanions. This possibility was accomplished with (trimethylcyclopropen-1-yl)(*p*-nitrophenyl)malononitrile(I) and (triphenylcyclopropen-1-yl)(*p*-nitrophenyl)malononitrile(II) that were prepared from their component ions and isolated as covalent compounds. The single-crystal X-ray structure of compound I indicates that an unusually long carbon-carbon bond exists between the incipient ionic fragments. Compounds I and II heterolyze to their ionic precursors upon solution in polar solvents. The effect of solvent dielectric constant and temperature variation on the coordination/heterolysis equilibria follow simple Born electrostatics. For the coordination reactions of five para-substituted arylmalononitrile carbanions with trimethyl- and triphenylcyclopropenium ions in acetonitrile, good linear correlations were found for free energies of reaction vs. enthalpies of reaction and also vs. free energies of protonation of the anions in Me₂SO. Proportionality between the enthalpies of coordination and carbanion redox potentials in acetonitrile was also found. Electron transfer appears to be an alternative pathway to coordination as suggested by isolation of dimers derived from the carbanions. The redox potentials for some of the carbanions and carbocations in acetonitrile were estimated from cyclic voltammetry. The results suggest that electron transfer is more sensitive to substituent variations than the coordination channel. This paper presents experimental details for the results previously communicated and also many new data.

Carbocations and carbanions are the two most important reactive species in organic chemistry. Despite the enormous importance of free radical chemistry, the great majority of ordinary synthetic reactions as well as those employed in industry involve the activation of neutral molecules by acids or bases to produce carbocations or carbanions as reactive intermediates that can engage in electrophilic or nucleophilic attack on other neutral species. However, there have been no systematic studies of simple coordination reactions between carbocations and carbanions, although related work indicates clearly that such a study should be feasible.

At first glance it would seem that these ionic species of carbon are so reactive that they could not be studied in the same medium. Since carbocations are usually produced in strongly acidic media and carbanions in strongly basic solutions, one might suppose that conditions for their coexistence would be hard to find. However, it has been known for many years that appropriately stabilized members of both species can exist across a wide part of the pH scale. For example, several of the triarylmethane dyes can exist as free carbocation species up to a pH of 8 and some of the cyanocarbon acids ionize spontaneously in aqueous solutions of greater than 1 M mineral acid.

A brief survey provides excellent reasons for believing that a broad scale investigation of carbocation-carbanion reactions should be feasible. The important studies by C. D. Ritchie and his students on the reactions of resonance-stabilized carbocations with a wide range of inorganic anions includes one of the simplest carbanions, the cyanide ion.¹ Many resonance-stabilized carbanions have basicities against protons in the same range as the anions studied by Ritchie's group. The NMR studies of Kessler² on ion pairing and ionization of stabilized carbocations with inorganic anions complement Ritchie's work and provide a rationale for predicting which systems will lead irreversibly to covalent products and which should come to simple equilibria between ions and covalent products. The spontaneous racemization of the

alkaloids regulovasine A and B may proceed through simple intramolecular heterolysis to a transient carbocation-carbanion pair followed by recoordination.³

The best guides presently available for predicting which systems give equilibria between stabilized free ions and covalent products are probably the pK_{R^+} of the cation and the pK_{HA} of the conjugate acid of the anion. Again, Kessler and his colleagues have limited their studies to inorganic anions that are not amenable to structural variation nor of direct relevance to carbanion chemistry. However, the rough success of their approach indicates at least a fair proportionality between the affinities of the anions toward solvated protons and toward delocalized carbocations.

Several investigators have been interested in the reactions between carbocations and anionic species in terms of the products that are formed. Vol'pin⁴ investigated the covalent products obtained by reacting a series of tropylium ions with various inorganic ions. Zaugg⁵ examined the products of triarylmethyl carbocations and several enolates derived from β -diketones. LeGoff and LaCount⁶ reported that a charge-transfer complex was produced rather than a covalent bond between the highly stabilized pentacarbethoxycyclopentadienyl anion and tropylium cation.

On the basis of these precedents, we tried various combinations of resonance-stabilized cations and anions. The results, presented in a preliminary communication,⁷ indicated that the rates of formation of covalent products are highly dependent upon the thermodynamic stabilities of both ions as represented by pK_{R^+} or pK_{HA} . If both ions are stabilized sufficiently, as in the case of crystal violet cation ($pK_{R^+} = 9.4$) with (*p*-nitrophenyl)malononitrile anion ($pK_{HA} = -1$ in Me₂SO, estimated) in acetonitrile, no detectable reaction was observable after 6 months standing. As the

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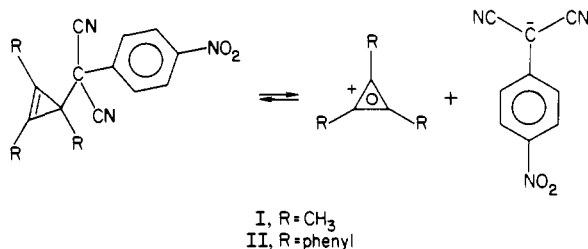
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thermodynamic stabilities of either or both ions was reduced, the rate of reaction between them increased, and in the limit, we would expect it to become diffusion controlled.

With such preliminary kinetic information in hand, two systems were found whose equilibria could be studied conveniently in solution. Trimethylcyclopropenium and triphenylcyclopropenium ions reacted cleanly with substituted phenylmalononitrile anions to produce covalent compounds that were isolated as white crystalline materials. A full single-crystal X-ray analysis⁸ of the covalent product I from reaction of trimethylcyclopropenium cation



and (*p*-nitrophenyl)malononitrile anion showed conclusively that it is a neutral covalent species. When dissolved in nonpolar solvents such as benzene, a colorless solution was formed. However, in more polar media, the deep red color of the (*p*-nitrophenyl)malononitrile anion appeared and its intensity was related cleanly to the solvent polarity. The free energies of heterolysis of I and II were correlated with the reciprocal dielectric constant of the medium in accordance with the Born equation. Thus, prototypical covalent compounds have been produced with carbon-carbon bonds that are so unstable relative to their component carbocations and carbanions that they may be heterolyzed simply by a change in solvent polarity. Although this is not a revolutionary finding, it is novel and offers an approach to the study of structural and medium effects on polar organic reactions since the usual complications from leaving groups are eliminated.

Experimental Section

Sources and Purification of Materials. Commercial solvents of the purest grade obtainable were dried, distilled, and handled under argon following standard recommended procedures. Center cuts (25–75%) from distillation were used and boiling points compared with literature values.

Carbanion Precursors. Acetylacetone (Aldrich) was vacuum distilled: bp 39–40 °C at 25 mm.

Dimethyl ethylmalonate was prepared by the method of Vogel⁹ from ethylmalonic acid and distilled prior to use: bp 160 °C at 739 mm.

Dimethyl methylmalonate was prepared from methylmalonic acid by Vogel's⁹ procedure and distilled: bp 171–175 °C at 728 mm.

Methyl dimedone (2,5,5-trimethylcyclohexane-1,3-dione) was prepared by methylating dimedone with methyl iodide in refluxing aqueous sodium hydroxide for 26 h.¹⁰ Upon cooling, the white product precipitated and was recrystallized from ethyl acetate: mp 158–159.6 °C.

Methyl Meldrum's acid (isopropylidene ethylmalonate) was prepared from the acidic condensation of methylmalonic acid with acetone in the presence of acetic anhydride.¹¹ The product was recrystallized from an acetone-water mixture: mp 113.2–114.0 °C.

Dibenzoylmethane (Aldrich) was purified¹² by recrystallization from petroleum ether and then from methanol to give white needles: mp 75–76 °C.

Dipivaloylmethane (Aldrich) was purified¹² by vacuum distillation: bp 83–86 °C at 6–10 mm.

Methylacetylacetone was prepared by refluxing acetylacetone with anhydrous potassium carbonate and methyl iodide in acetone for 4–6 h:¹³ bp 68–72 °C at 26 mm.

Ethylacetylacetone was prepared by refluxing acetylacetone with anhydrous potassium carbonate and ethyl iodide in acetone for 4–6 h:¹³ bp 73–74 °C at 26 mm.

Ethyl dimedone (3,3-dimethyl-6-ethylcyclohexane-1,5-dione) was prepared from 3,3-dimethylglutaric acid¹⁴ by using sodium ethoxide for the ring closure of ethyl 3,3-dimethyl-5-ke'ooctanoate to ethyl dimedone. Ethyl dimedone was recrystallized from water-methanol (1:1 by volume), yielding white crystals: mp 156.5–159 °C; ¹H NMR (Me₂SO-*d*₆) δ 2.18 (s, 4 H, ring methylene), 2.17 (q, 2 H, CH₂ of ethyl group), 0.96 (s, 6 H, methyls), 0.825 (t, 3 H, CH₃ of ethyl group).

Ethyl Meldrum's acid (isopropylidene ethylmalonate) was prepared from ethylmalonic acid and acetone as described by Abramovitch:¹¹ mp 107.5–108.0 °C.

(*p*-Nitrophenyl)malononitrile was prepared from (*p*-nitrophenyl)acetonitrile by adding cyanogen chloride to a sodium hydride mixture of (*p*-nitrophenyl)acetonitrile in dried tetrahydrofuran according to the procedure of Hartzler.¹⁵ After neutralization of the carbanion to its acid, the product was recrystallized from benzene-hexane, yielding pale yellow needles: mp 110.0–110.7 °C; ¹H NMR (CDCl₃) δ 5.22 (s, 1 H), 7.70, 7.81, 8.33, 8.44 (AA'BB', 4 H). Anal. Calcd for C₉H₅N₃O₂: C, 57.76; H, 2.69; N, 22.45; O, 17.10. Found: C, 57.74; H, 2.85; N, 22.04.

(*p*-Chlorophenyl)malononitrile was prepared by slowly adding 10.9 g (0.0718 mol) of (*p*-chlorophenyl)acetonitrile (Aldrich) in 200 mL of dry tetrahydrofuran to 5.74 g (0.0718 mol) of sodium hydride (60% dispersion in mineral oil, Aldrich) in 100 mL of dry tetrahydrofuran under argon. The reaction mixture was refluxed for 1 h and allowed to cool to room temperature. While the reaction mixture was cooled with an ice bath, 9.0 g (0.076 mol) of phenyl cyanate was added slowly to the reaction mixture by using a syringe, and the reaction was allowed to warm to room temperature overnight. The reaction mixture was poured carefully into a beaker containing ice water and neutralized with 6 N HCl. The aqueous phase was extracted with ether (2 × 100 mL). The product was extracted from the ethereal layer with saturated sodium bicarbonate (3 × 100 mL), the aqueous layer neutralized with 6 N HCl, and the product reextracted with ether. The ethereal layer was dried with anhydrous sodium sulfate, and the ether was removed by rotoevaporation. The product was recrystallized from cyclohexane, yielding white crystals: mp 70.5–70.7 °C (lit.¹⁶ mp 70.2–70.7 °C); ¹H NMR (CDCl₃) δ 5.03 (s, 1 H), 7.46 (s, 4 H). Anal. Calcd for C₉H₅N₂Cl: C, 61.21; H, 2.85; N, 15.86; Cl, 20.07. Found: C, 61.20; H, 3.11; N, 15.76; Cl, 19.94.

(*p*-Cyanophenyl)malononitrile, (*p*-methylphenyl)malononitrile, (*p*-methoxyphenyl)malononitrile, and phenylmalononitrile were all prepared following the procedure for the preparation of (*p*-chlorophenyl)malononitrile. However, these arylmalononitriles were refluxed overnight with NaH before adding the phenyl cyanate. In the case of (*p*-methoxyphenyl)malononitrile, the product was purified by column chromatography from silica gel (Eastman) using chloroform as eluent.

(*p*-Cyanophenyl)malononitrile: mp 105.0–106.0 °C; ¹H NMR (CDCl₃) δ 5.10 (s, 1 H), 7.54, 7.64, 7.71, 7.82 (AA'BB', 4 H). Anal. Calcd for C₁₀H₅N₃: C, 71.85; H, 3.01; N, 25.14. Found: C, 72.00; H, 3.07; N, 25.16.

(*p*-Methylphenyl)malononitrile: mp 57.0–57.4 °C (lit.¹⁶ mp 57.0–57.5 °C); ¹H NMR (CDCl₃) δ 2.36 (s, 3 H), 5.04 (s, 1 H), 7.17, 7.28, 7.30, 7.41 (AA'BB', 4 H). Anal. Calcd for C₁₀H₈N₂: C, 76.90; H, 5.16; N, 17.94. Found: C, 77.06; H, 5.35; N, 17.70.

(*p*-Methoxyphenyl)malononitrile: mp 61.2–61.9 °C; ¹H NMR (CDCl₃) δ 3.83 (s, 3 H), 4.99 (s, 1 H), 6.92, 7.03, 7.35, 7.45 (AA'BB', 4 H). Anal. Calcd for C₁₀H₈N₂O: C, 69.76; H, 4.68; N, 16.27; O, 9.29. Found: C, 69.88; H, 4.83; N, 16.26.

Phenylmalononitrile: mp 67.7–68.0 °C (lit.¹⁷ mp 66–68 °C); ¹H NMR (CDCl₃) δ 5.07 (s, 1 H), 7.49 (s, 5 H). Anal. Calcd for C₉H₆N₂: C, 76.04; H, 4.25; N, 19.71. Found: C, 76.28; H, 4.44; N, 19.46.

Phenyl cyanate was prepared from phenol and cyanogen bromide following the procedure of Zweifel.¹⁸

Carbanion Salts. The alkali-metal enolate salts were prepared under argon by adding the appropriate alkali metal to 25 mL of freshly distilled methanol containing a small amount of benzene. To the resulting methoxide solution was added an equimolar amount of β-dicarbonyl compound. After approximately 15 min, the solution was evaporated to dryness on a rotary evaporator, washed with benzene, and filtered. The enolates were dried by pumping and stored in the dark in a vacuum desiccator at room temperature and a pressure of less than 1 torr for 24 h before use. No enolate was kept longer than 2 weeks. Due to the hygroscopic nature of these salts and their Me₂SO solutions, all labora-

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tory manipulations were performed under argon.

Arylmalononitrile salts were usually prepared by adding 1 equiv of potassium metal to 25 mL of freshly dried methanol under argon, followed by 1 equiv of the appropriate carbon acid. After 15 min, the methanol was removed by rotoevaporation and pumping. The carbanion salt was stored immediately in a vacuum dessicator until use. All laboratory operations involving the carbanion salts were carried out under argon, since only the (*p*-nitrophenyl)malononitrile anion salts are stable to air. Only the stable (*p*-nitrophenyl)malononitrile salts gave satisfactory elemental analyses.

The potassium salt of (*p*-chlorophenyl)malononitrile: $^1\text{H NMR}$ (CD_3CN) δ 7.14, 7.03, 6.91, 6.82 (AA'BB', 4 H); UV-vis (CH_3CN) λ_{max} 308 nm (ϵ 2.57×10^4).

The potassium salt of (*p*-cyanophenyl)malononitrile: $^1\text{H NMR}$ (CD_3CN) δ 7.35, 7.24, 6.93, 6.82 (AA'BB', 4 H); UV-vis (CH_3CN) λ_{max} 357 nm (ϵ 4.52×10^4).

The potassium salt of (*p*-methylphenyl)malononitrile: $^1\text{H NMR}$ (acetone- d_6) δ 6.78 (s, 4 H), 2.13 (s, 3 H); UV-vis (CH_3CN) λ_{max} 298 nm (ϵ 2.17×10^4). Methylation of the carbanion with methyl iodide gave carbon alkylation: $^1\text{H NMR}$ (acetone- d_6) δ 7.64, 7.53, 7.44, 7.33 (AA'BB', 4 H), 2.39 (s, 3 H), 2.21 (s, 3 H).

The potassium salt of (*p*-methoxyphenyl)malononitrile: $^1\text{H NMR}$ (CD_3CN) δ 6.76 (br s, 4 H), 3.69 (s, 3 H); UV-vis (CH_3CN) λ_{max} 293 nm (ϵ 2.07×10^4).

The potassium salt of phenylmalononitrile: $^1\text{H NMR}$ (CD_3CN) δ 6.5–7.2 (m, 5 H); UV-vis (CH_3CN) λ_{max} 298 nm (ϵ 2.20×10^4).

The potassium salt of (*p*-nitrophenyl)malononitrile was also prepared by dissolving 369 mg of KOH pellets in 20 mL of deionized water. Then 1.046 g of (*p*-nitrophenyl)malononitrile was added followed by 10 mL of ethanol to form a dark red solution. The solution was warmed until all the carbon acid dissolved and was then cooled with an ice bath until blue crystals precipitated. They were recrystallized from acetonitrile: $^1\text{H NMR}$ (acetone- d_6) δ 7.93, 7.81, 6.90, 6.78 (AA'BB', 4 H); UV-vis (CH_3CN) λ_{max} 475 nm (ϵ 3.01×10^4). Anal. Calcd for $\text{C}_9\text{H}_4\text{N}_2\text{O}_2\text{K}$: C, 47.99; H, 1.79; N, 18.66; K, 17.36. Found: C, 47.91; H, 2.01; N, 18.44; K, 17.26.

The tetra-*n*-butylammonium salt of (*p*-nitrophenyl)malononitrile was prepared from (*p*-nitrophenyl)malononitrile and tetra-*n*-butylammonium hydroxide. To a 25-mL round-bottomed flask were added 187 mg of (*p*-nitrophenyl)malononitrile, 644 mg of tetra-*n*-butylammonium hydroxide (40% wt solution, Aldrich), and 12 mL of deionized water. Then 10 mL of ethanol was added and the temperature raised to 50 °C. After the carbon acid dissolved, the clear, red solution was allowed to cool slowly to room temperature yielding red needles that were filtered and washed with deionized water: mp 114.5–116.5 °C; $^1\text{H NMR}$ (acetone- d_6) δ 7.92, 7.80, 6.89, 6.78 (AA'BB', 4 H); UV-vis (CH_3CN) λ_{max} 475 nm (ϵ 3.08×10^4). Anal. Calcd for $\text{C}_{25}\text{H}_{40}\text{N}_4\text{O}_2$: C, 70.06; H, 9.41; N, 13.07. Found: C, 70.20; H, 9.25; N, 12.92.

Preparation and Sources of Electrophiles. Tri-*p*-tolylmethyl alcohol was prepared from the Grignard reaction of *p*-tolylmagnesium bromide and methyl *p*-toluate ester. The product was recrystallized from heptane-methylene chloride (50/50 volume), yielding a white solid: mp 94–96 °C (lit.⁵ mp 93–95 °C).

Tri-*p*-tolylmethyl tetrafluoroborate was prepared according to either the procedure of Zaugg⁵ or the procedure of Dauben¹⁹ and was isolated as a yellow salt: $^1\text{H NMR}$ (CDCl_3) δ 7.72, 7.60, 7.58, 7.48 (AA'BB', 12 H), 2.67 (s, 9 H).

Tri-*p*-anisylmethyl alcohol was prepared from the Grignard reaction of *p*-anisylmagnesium bromide and methyl *p*-methoxybenzoate ester. The crude product was recrystallized from heptane-methylene chloride (50/50 volume), yielding a white solid: mp 81–83 °C (lit.²⁰ mp 82.5 °C).

Tri-*p*-anisylmethyl tetrafluoroborate was prepared according to the procedure of Dauben¹⁹ and was isolated as a red salt: $^1\text{H NMR}$ (CDCl_3) δ 7.62, 7.52, 7.32, 7.22 (AA'BB', 12 H), 4.10 (s, 9 H).

Crystal violet chloride (Fisher) was used as received.

Malachite green tetrafluoroborate and Crystal violet tetrafluoroborate were prepared by Ritchie's procedure.²¹

Triphenylcyclopropenium tetrafluoroborate was prepared from triphenylcyclopropene (Alfa) by the Dauben hydride abstraction method¹⁹ and was recrystallized from acetonitrile, yielding white needles: mp over 250 °C. Anal. Calcd for $\text{C}_{21}\text{H}_{15}\text{BF}_4$: C, 71.22; H, 4.27. Found: C, 71.18; H, 4.13.

Trimethylcyclopropenium tetrafluoroborate was prepared by using a procedure described by Closs.²² The salt was recrystallized by dissolving

in acetone and leaving it in a covered vessel containing ether, yielding white needles: mp 129–132 °C (lit.²² mp 132–134 °C).

Tropylum tetrafluoroborate (Aldrich) was recrystallized from acetonitrile-ether as a white solid: $^1\text{H NMR}$ (CD_3CN) δ 9.25 (s, 7 H).

Preparation of Carbanion-Carboxylic Products. All substituted cyclopropenyl-substituted phenylmalononitrile covalent products were prepared as follows: to a dry flask under positive argon pressure were added 1 mmol of the potassium salt of substituted phenylmalononitrile, 1 mmol of substituted cyclopropenium tetrafluoroborate, and 10 mL of spectrophotometric grade acetone. The resulting solution was stirred for 15 min. Then 10 mL of diethyl ether was added and the solution filtered to remove KBF_4 . After the solvents were removed by rotoevaporation and pumping, the residue was recrystallized.

(Triphenylcyclopropenyl)(*p*-nitrophenyl)malononitrile: mp 152.8–154.0 °C (from benzene-hexane; decomposes to red liquid); IR (KBr pellet) 2250 (w, nitrile), 1830 (w, cyclopropene), no absorbance at 2010 cm^{-1} (s, ketene imine); $^1\text{H NMR}$ (acetone- d_6) δ 7.48–8.22 (m, ArH); $^{13}\text{C NMR}$ (CDCl_3 at -40 °C) δ 147.6, 138.1, 137.3, 130.3, 129.6, 129.1, 128.6, 128.3, 125.5, 123.4 (aromatic carbons), 115.5 (cyclopropene olefinic carbons), 114.3 (nitrile carbons), 48.1 (CN- ^{13}C -CN), 43.3 (quaternary cyclopropene carbon). Anal. Calcd for $\text{C}_{30}\text{H}_{19}\text{N}_3\text{O}_2$: C, 79.46; H, 4.22; N, 9.27; O, 7.06. Found: C, 79.71; H, 4.22; N, 9.12; O, 7.17.

(Triphenylcyclopropenyl)(*p*-cyanophenyl)malononitrile: mp 194.2–194.8 °C (from benzene-hexane); IR (PAS, neat powder) 2237 (s, nitrile), 1825 (w, cyclopropene), no absorbance at 2010 cm^{-1} (s, ketene imine); $^1\text{H NMR}$ (CDCl_3) δ 7.36–7.75 (m, ArH). Anal. Calcd for $\text{C}_{31}\text{H}_{19}\text{N}_3$: C, 85.89; H, 4.42; N, 9.69. Found: C, 86.03; H, 4.55; N, 9.59.

(Triphenylcyclopropenyl)(*p*-methylphenyl)malononitrile: mp 158–159 °C (from benzene-hexane); IR (KBr pellet) 2240 (w, nitrile), 1800 (w, cyclopropene), no absorbance at 2010 cm^{-1} (s, ketene imine); $^1\text{H NMR}$ (acetone- d_6) δ 7.00–7.90 (m, 15 H), 2.12 (s, 3 H); $^{13}\text{C NMR}$ (CDCl_3) δ 139.6, 130.0, 129.1, 128.4, 127.9, 127.5, 127.0 (aromatic carbons), 116.7 (cyclopropene olefinic carbons), 115.8 (nitriles), 48.7 (CN- ^{13}C -CN), 43.7 (quaternary cyclopropene carbon), 20.9 (ArCH₃). Anal. Calcd for $\text{C}_{31}\text{H}_{22}\text{N}_2$: C, 88.12; H, 5.25; N, 6.63. Found: C, 88.06; H, 5.31; N, 6.57.

(Trimethylcyclopropenyl)(*p*-nitrophenyl)malononitrile: mp 101.0–101.5 °C (from cyclohexane; decomposes to dark red liquid); IR (KBr pellet) 2230 (w, nitrile), 1830 (w, cyclopropene), no absorbance at 2010 cm^{-1} (s, ketene imine); $^1\text{H NMR}$ (CDCl_3 at -50 °C) δ 2.07 (s, 6 H), 1.29 (s, 3 H); $^{13}\text{C NMR}$ (CDCl_3 at -50 °C) δ 147.7, 138.7, 127.5, 124.4 (aromatic carbons), 115.7 (cyclopropene olefinic carbons), 114.5 (nitrile carbons), 50.6 (CN- ^{13}C -CN), 35.5 (cyclopropene carbon), 18.6 (cyclopropene methyl), 8.8 (cyclopropene methyl). Anal. Calcd for $\text{C}_{15}\text{H}_{13}\text{N}_3\text{O}_2$: C, 67.40; H, 4.90; N, 15.72. Found: C, 67.28; H, 5.02; N, 15.61.

(Trimethylcyclopropenyl)(*p*-chlorophenyl)malononitrile: mp 80.0–80.8 °C (from hexane); IR (KBr pellet) 2245 (s, nitrile), 1867 (w, cyclopropene), no absorbance at 2010 cm^{-1} (s, ketene imine); $^1\text{H NMR}$ (CDCl_3) δ 7.40 (s, 4 H), 2.01 (s, 6 H), 1.23 (s, 3 H). Anal. Calcd for $\text{C}_{15}\text{H}_{13}\text{N}_2\text{Cl}$: C, 70.18; H, 5.10; N, 10.91; Cl, 13.81. Found: C, 70.41; H, 5.28; N, 11.04; Cl, 14.03.

(Trimethylcyclopropenyl)(*p*-cyanophenyl)malononitrile: mp 74.5–75.5 °C (from benzene-hexane); IR (KBr pellet) 2235 (s, nitrile), 1865 (w, cyclopropene), no absorbance at 2010 cm^{-1} (s, ketene imine); $^1\text{H NMR}$ (CDCl_3) δ 7.83, 7.72, 7.62, 7.52 (AA'BB', 4 H), 1.87 (br s, 9 H). Anal. Calcd for $\text{C}_{16}\text{H}_{13}\text{N}_3$: C, 77.71; H, 5.30; N, 16.99. Found: C, 77.62; H, 5.36; N, 16.92.

(Trimethylcyclopropenyl)(*p*-methylphenyl)malononitrile: mp 65.7–66.2 °C (from pentane); IR (KBr pellet) 2243 (s, nitrile), 1864 (w, cyclopropene), no absorbance at 2010 cm^{-1} (s, ketene imine); $^1\text{H NMR}$ (CDCl_3) δ 7.28, 7.25 (4 H), 2.38 (s, 3 H), 2.01 (s, 6 H), 1.21 (s, 3 H). Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{N}_2$: C, 81.32; H, 6.82; N, 11.85. Found: C, 81.58; H, 6.94; N, 12.03.

(Trimethylcyclopropenyl)(*p*-methoxyphenyl)malononitrile: mp 50.6–51.4 °C (from hexane); IR (KBr pellet) 2245 (s, nitrile), 1867 (w, cyclopropene), no absorbance at 2010 cm^{-1} (s, ketene imine); $^1\text{H NMR}$ (CDCl_3) δ 7.41, 7.30, 6.99, 6.88 (AA'BB', 4 H), 3.83 (s, 3 H), 2.02 (s, 6 H), 1.22 (s, 3 H). Anal. Calcd for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}$: C, 76.16; H, 6.39; N, 11.10; O, 6.34. Found: C, 76.33; H, 6.42; N, 11.24.

(Trimethylcyclopropenyl)phenylmalononitrile: mp 38.4–39.0 °C (from hexane); IR (KBr pellet) 2245 (s, nitrile), 1870 (w, cyclopropene), no absorbance at 2010 cm^{-1} (s, ketene imine); $^1\text{H NMR}$ (CDCl_3) δ 7.37 (s, 5 H), 1.95 (s, 6 H), 1.14 (s, 3 H). Anal. Calcd for $\text{C}_{15}\text{H}_{14}\text{N}_2$: C, 81.05; H, 6.35; N, 12.60. Found: C, 80.86; H, 6.36; N, 12.73.

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4-(Tri-*p*-tolylmethyl)-2,2,6,6-tetramethyl-3,5-heptanedione was prepared by adding 202 mg of sodium dipivaloylmethide and 365 mg of tri-*p*-tolylmethyl tetrafluoroborate to a 25-mL round-bottom flask purged with argon. Then 15 mL of dry acetonitrile was added, and the solution was stirred for 1 h. The reaction mixture was worked up by adding 15 mL of water and 15 mL of diethyl ether. The ethereal layer was separated, washed with water, and dried with anhydrous magnesium sulfate and the ether removed by rotoevaporation. The resulting syrupy solid was recrystallized from 10 mL of methanol, yielding colorless prisms: mp 156–159 °C (lit.⁵ mp 156–157 °C).

4-Tropyl-2,2,6,6-tetramethyl-3,5-heptanedione was prepared by adding 1.002 g of sodium dipivaloylmethide to a 25-mL round-bottom flask followed by 12 mL of purified Me₂SO under nitrogen. The reaction was stirred as 0.864 g of tropylium tetrafluoroborate was added resulting in a red-brown solution. After 30 min, 20 mL of water and 25 mL of diethyl ether were added to the reaction. The ethereal layer was separated, washed twice with water, and dried with anhydrous magnesium sulfate and the ether removed by rotoevaporation. The white residue was recrystallized from aqueous methanol, yielding colorless needles: mp 94.0–95.0 °C; ¹H NMR (CDCl₃) δ 6.62 (t, 2 H, *J* = 3 Hz, cycloheptatriene), 6.22 (t, 1 H, *J* = 3 Hz, cycloheptatriene), 6.10 (t, 1 H, *J* = 3 Hz, cycloheptatriene), 5.30 (d, 1 H, *J* = 6 Hz, cycloheptatriene), 5.19 (d, 1 H, *J* = 6 Hz, cycloheptatriene), 4.85 (d, 1 H, *J* = 6 Hz, COCH₃), 2.57 (q, 1 H, cycloheptatriene), 1.14 (s, 18 H, CCH₃).

The dimer of (*p*-nitrophenyl)malononitrile (1,2-bis(*p*-nitrophenyl)-1,1,2,2-tetracyanoethane) was prepared according to the procedure of Hartzler.²³ Filtration of the crude product and recrystallization from 1,2-dichloroethane gave colorless crystals: mp 157.5–159 °C (lit.²³ crude mp 149–150 °C, from 1,2-dichloroethane mp 164–166 °C).

Spectroscopy. All ¹H NMR spectra were recorded on either a JEOL FX90Q or an IBM NR80. All ¹³C NMR spectra were recorded on either a JEOL FX60 or JEOL FX90Q. Chemical shifts are reported in parts per million relative to tetramethylsilane. IR spectra were recorded on either an IBM IR/95 or a Perkin-Elmer 297. All electronic spectra were recorded on a Cary 15 spectrophotometer equipped with a thermostated cell-holder. The temperature was monitored by using a calibrated thermistor that was placed between the cell and cell holder and was controlled easily within ±0.2 °C.

Equilibrium Constants for the (*p*-Nitrophenyl)malononitrile–Triphenylcyclopropene System in Several Solvents. Solutions were prepared by weighing 20–30 mg of pale yellow covalent crystals into a 25-mL volumetric flask. Then solvent was added with a syringe while the flasks were purged with argon. The cuvette cell was then rinsed at least three times with solution, filled, and placed in the spectrophotometer for 15 min in order to reach thermal equilibrium. Equilibrium constants were obtained by monitoring the absorbance of the (*p*-nitrophenyl)malononitrile anion (λ_{max} 475 nm (ε 30 000)) using either a 1.00-mm or 1.00-cm cell. Triphenylcyclopropenium ion and the covalent compound do not absorb light in this region of the visible spectrum. Equilibrium constants were checked occasionally at different initial concentrations of covalent crystals.

Beer's law behavior of (*p*-nitrophenyl)malononitrile anion was determined in each solvent by using the potassium or tetra-*n*-butylammonium salt. The stability of each solution was checked by occasionally recording the spectra again after a few hours. Only cyclohexanone and 4-methyl-2-pentanone gave unstable carbanion solutions. The carbanion decomposes slowly in these solvents making it necessary to calculate the molar absorptivity coefficients by extrapolation back to the time of mixing. For the worst case, only a 15% decrease in absorbance was observed per 1 h. The molar absorptivity coefficients of the carbanion in all solvents were between 3.01 × 10⁴ (acetonitrile) and 3.51 × 10⁴ (acetone) with the wavelength of maximum absorbance varying between 475 (acetonitrile) and 495 nm (cyclohexanone).

The equilibrium constant for heterolysis/coordination in acetonitrile was also determined by starting with the (*p*-nitrophenyl)malononitrile carbanion salt and triphenylcyclopropenium tetrafluoroborate. Equilibrium constants were determined at several different initial ratios of carbocation and carbanion concentrations and at constant ionic strength by using a swamping electrolyte solution of 1.307 × 10⁻² M tetra-*n*-butylammonium tetrafluoroborate.

Equilibrium solutions were prepared by adding weighed amounts of stock carbanion solution (2.13 × 10⁻³ M) and carbocation solution (9.02 × 10⁻⁴ M) to a 10-mL volumetric flask and filling to the 10-mL mark with a weighed amount of swamping electrolyte solution. The equilibrium constant for heterolysis was determined by measuring the absorbance of the (*p*-nitrophenyl)malononitrile carbanion.

Calorimetry. Heats of reaction were measured by using a Tronac Model 1250 calorimeter operated in the isoperibol mode at 25 °C. Since

many of the arylmalononitrile salt solutions are unstable on exposure to air, calorimetry solutions were used within 2 h of preparation.

Heats of reaction were determined by measuring the pen displacement on a strip chart recorder in series with the thermistor and were calibrated before and after every heat of reaction measurement by passing electrical current through the calibration heater for known time intervals and measuring the change in temperature as detected on the strip chart recorder.

At concentrations above 2 mM, KBF₄ precipitates out of acetonitrile. The precipitation of KBF₄ was detected readily in the thermograms and was eliminated by using concentration of reactants below or equal to 2 mM.

The heat of dilution of triphenylcyclopropenium tetrafluoroborate was shown to be small enough to be neglected for heat of reaction measurements.

Cyclic Voltammetry. A Princeton Applied Research Co. (PARC) Model No. 175 universal programmer was used to vary the applied potential that was provided by a PARC Model 173 potentiostat. The electrometer was a PARC Model No. 178. The reference, working, and auxiliary electrodes were positioned in an air-tight vessel (IBM Instruments) equipped with a nitrogen inlet. The Ag/Ag⁺ reference electrode was prepared by using 0.1 M AgNO₃ acetonitrile solution (EGG, PARC). The working electrode was either a platinum disk (Corning, platinum inlay, Cat. No. 476060) or glassy carbon (Bioanalytical Systems, Inc.). The auxiliary electrode was platinum wire or platinum disk. The potential of the Ag/Ag⁺ reference electrode relative to the SCE was 0.353 V.²⁴

Carbocation and carbanion solutions (2 mM) were prepared by dissolving 20–25 mg of potassium arylmalononitrile salts under argon into 25 mL of supporting electrolyte (0.160 M tetra-*n*-butylammonium tetrafluoroborate).

Cyclic voltammograms were obtained by first determining the peak potential of interest, stirring the solution, and then recording the cyclic voltammogram starting at an initial potential at least 200 mV away from the peak potential being measured. The voltammograms were also recorded at several different scan rates. Since the carbocations and arylmalononitrile salts exhibited irreversible electrochemical behavior, the reported potential values, unless otherwise stated, correspond to peak potentials relative to the potential of ferrocene in acetonitrile. The potential of a prepared standard 2.5 mM ferrocene solution in acetonitrile was measured against the Ag/Ag⁺ reference electrode before and after the cyclic voltammetry experiment.

Results

The Combination of Carbanions with Carbocations. The results for the combination of a variety of salts with carbocations in solution were presented in an earlier communication⁷ and have been extended to the substituted cyclopropenylarylmalononitriles in Table I. The carbocations and carbanions are listed according to their stabilities relative to their respective neutral precursors as indicated by p*K*_R⁺ (in H₂O) and p*K*_{HA} (in Me₂SO) values.

All covalent products shown in Table I were isolated and characterized as described in the Experimental Section. In addition, the single-crystal X-ray structure for (*p*-nitrophenyl)malononitrile–trimethylcyclopropene was reported.⁸ This establishes the structure of a model covalent carbanion–carbocation product.

For the covalent products reported in ref 7 only 4-(tri-*p*-tolylmethyl)-2,2,6,6-tetramethyl-3,5-heptanedione and 4-tropyl-2,2,6,6-tetramethyl-3,5-heptanedione, which were formed by reacting sodium dipivaloylmethide with tri-*p*-tolylmethyl carbocation and tropylium ion respectively, were isolated.

In cases where covalent products could not be isolated readily, covalent bond formation was determined by visually monitoring the disappearance of the triarylmethyl carbocation dyes and/or determined by comparing the ¹H NMR spectra to the spectra of other related products that had been isolated and well characterized.

For example, in acetonitrile the ¹H NMR spectra for (*p*-nitrophenyl)malononitrile carbanion reacting with tri-*p*-anisylmethyl carbocation showed both the covalent product and ionic forms of the carbocation, with the signals for the carbocation shifted downfield relative to the covalent product. Although the signal intensity for the carbanion was too weak to be detected by

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Table I. Thermodynamic Properties for Heterolysis of Covalent Products to Para-Substituted Phenylmalononitrile Carbanions and Substituted Cyclopropenium Carbocations in Acetonitrile at 25 °C ($\Delta G_{\text{het}}^{\circ}$ and $\Delta H_{\text{het}}^{\circ}$ in kcal mol⁻¹; $\Delta S_{\text{het}}^{\circ}$ in cal mol⁻¹ deg⁻¹)

carbanions		carbocations					
X	pK _{HA}	$\Delta G_{\text{het}}^{\circ}$	$\Delta H_{\text{het}}^{\circ}$	$\Delta S_{\text{het}}^{\circ}$	$\Delta G_{\text{het}}^{\circ}$	$\Delta H_{\text{het}}^{\circ}$ ^a	$\Delta S_{\text{het}}^{\circ}$
NO ₂		5.39 ± 0.03 ^b	6.3 ± 0.3	3.0 ± 1.0	2.76 ± 0.10 ^c		
CN		7.00 ± 0.16	8.2 ± 0.3	4.0 ± 1.1	4.37 ± 0.05	4.3 ± 0.3	-0.1 ± 1.0
Cl	3.14		11.3 ± 0.3		7.87 ± 0.31	7.3 ± 0.3	-1.8 ± 1.4
H	4.24		12.2 ± 0.3		9.44 ± 0.15	8.5 ± 0.3	-3.1 ± 1.1
CH ₃	4.85		13.4 ± 0.3		10.32 ± 0.20	9.6 ± 0.3	-2.5 ± 1.2
OCH ₃	5.68		14.0 ± 0.3			10.9 ± 0.3	

^a Corrected for heat of dilution of the cation = -0.47 kcal/mol. ^b Compound II. ^c Compound I.

Table II. Tabulation of All Equilibrium Constants for Heterolysis Starting with Solutions of Covalent Compound II at 25 °C

solvent	dielectric const (25 °C)	initial concn, mM	ionic strength, m	K_{het}	γ_{\pm}^2	K_{het}°	$\Delta G_{\text{het}}^{\circ}$, kcal/mol
acetonitrile	35.95	0.188	1.37 × 10 ⁻⁴	1.38 × 10 ⁻⁴	0.925	1.28 × 10 ⁻⁴	5.39 ± 0.03
		0.781	3.36 × 10 ⁻⁴	1.31 × 10 ⁻⁴	0.885	1.16 × 10 ⁻⁴	
		1.05	3.97 × 10 ⁻⁴	1.28 × 10 ⁻⁴	0.876	1.12 × 10 ⁻⁴	
		3.36	7.85 × 10 ⁻⁴	1.35 × 10 ⁻⁴	0.829	1.12 × 10 ⁻⁴	
acetone	20.70	1.23	1.54 × 10 ⁻⁴	1.32 × 10 ⁻⁵	0.827	1.09 × 10 ⁻⁵	6.82 ± 0.03
		0.401	4.14 × 10 ⁻⁵	4.21 × 10 ⁻⁶	0.878	3.70 × 10 ⁻⁶	
cyclohexanone	18.3 ^a	0.0400	1.07 × 10 ⁻⁵	3.42 × 10 ⁻⁶	0.936	3.20 × 10 ⁻⁶	7.46 ± 0.12
		2.28	1.06 × 10 ⁻⁴	4.61 × 10 ⁻⁶	0.812	3.74 × 10 ⁻⁶	
		6.38	1.10 × 10 ⁻⁵	3.34 × 10 ⁻⁸	0.792	2.65 × 10 ⁻⁸	
4-methyl-2-pentanone	13.11 ^a	2.71	5.99 × 10 ⁻⁵	8.54 × 10 ⁻⁷	0.789	6.73 × 10 ⁻⁷	8.48 ± 0.12
1,2-dichloroethane	10.36	3.27	1.22 × 10 ⁻⁵	7.06 × 10 ⁻⁸	0.826	5.83 × 10 ⁻⁸	9.91 ± 0.03
methylene chloride	8.93	0.620	2.94 × 10 ⁻⁶	2.43 × 10 ⁻⁸	0.887	2.15 × 10 ⁻⁸	10.43 ± 0.05
		1.58	5.08 × 10 ⁻⁶	2.84 × 10 ⁻⁸	0.854	2.42 × 10 ⁻⁸	

^a 20 °C.

¹H NMR, it has been detected independently under the same reaction conditions by cyclic voltammetry. However, in THF-*d*₈, only the covalent product was detected. Alternatively, equilibrium could be approached from the covalent product by adding CD₃CN to the THF-*d*₈ solution containing covalent product.

Evidence of Equilibria. For most of the isolated covalent products derived from the phenylmalononitriles shown in Table I, equilibrium with their ionic precursors was confirmed by low-temperature ¹H and ¹³C NMR and by the visual or spectrophotometric detection of the carbanion upon dissolving the pale yellow covalent crystals in polar solvents.

For the formation of I starting from its ionic precursors in CDCl₃, both ¹H and ¹³C NMR spectra showed time averaging of the cyclopropene signals due to rapid equilibrium between the covalent product and its ionic precursors. The ¹H NMR spectrum at 25 °C consisted of one broad signal at 1.88 ppm for the cyclopropenium ion, which at -50 °C was resolved into two signals at 2.07 and 1.29 ppm corresponding to the covalent cyclopropene. At -50 °C, the ¹³C NMR spectrum confirmed covalent bond formation. However, at -10 °C the cyclopropene signals broadened and disappeared due to time averaging. Closs has reported analogous time-averaged behavior for ¹H NMR spectra of trimethylcyclopropene azide in CDCl₃.²⁵

Similar time-averaged behavior was observed by ¹³C NMR for II in CDCl₃ at +25 and -50 °C. The important observation that the (*p*-methylphenyl)malononitrile-triphenylcyclopropene system does not exhibit detectable time averaging at 25 °C indicates that the degree of stabilization of the carbanion has a great effect on the position of the ionic-covalent equilibrium.

For the crystal violet chloride and (*p*-nitrophenyl)malononitrile system no reaction had occurred, as determined by ¹H NMR, after over 6 months.

The less stable arylmalononitrile salts and less stable carbocations react to give dimerization products. The carbanion dimers

were isolated easily as they precipitated from reaction solution.

The Determination of Equilibrium Constants. Table I presents the standard free energies, enthalpies, and entropies of coordination/heterolysis for various substituted arylmalononitrile carbanion-cyclopropenium cation combinations.^{8b}

The preparation of solutions for equilibrium constants and the required instrumentation are described in the Experimental Section. Equilibrium constants for heterolysis were approached from solutions of the covalent crystals and/or by the combination of ions. They were calculated from initial concentrations and the equilibrium carbanion concentration by using the molar absorbance values. Concentration equilibrium constants for heterolysis, K_{het} , were calculated by using eq 1-5, where [A⁻] is the concentration of anion of extinction coefficient ϵ , [C⁺] is the concentration of the carbocation, [A-C] is the concentration of covalent compound, and Abs is the measured absorbance of the equilibrium solution.

$$A-C \rightleftharpoons A^- + C^+ \quad (1)$$

$$[A^-]_{\text{eq}} = \text{Abs}/\epsilon \quad (2)$$

$$[C^+]_{\text{eq}} = [C^+]_{\text{init}} - ([A^-]_{\text{init}} - [A^-]_{\text{eq}}) \quad (3)$$

$$[A-C]_{\text{eq}} = [A-C]_{\text{init}} + ([A^-]_{\text{init}} - [A^-]_{\text{eq}}) \quad (4)$$

$$K_{\text{het}} = [A^-]_{\text{eq}}[C^+]_{\text{eq}}/[A-C]_{\text{eq}} \quad (5)$$

Thermodynamic equilibrium constants, K_{het}° (molarity), were calculated by using eq 6. Activity coefficients for the covalent

$$K_{\text{het}}^{\circ} = K_{\text{het}}(\gamma_{\pm})^2 \quad (6)$$

product were assumed to be unity. The mean activity coefficients, γ_{\pm} (molarity standard state), for the carbanion and carbocation were calculated by using the Debye-Hückel limiting law equation.

Table II contains the equilibrium constants of heterolysis of compound II determined in several solvents as approached from solutions of the covalent crystals at 25 °C. The equilibrium constant for heterolysis in CH₃CN was also checked by ap-

Table III. Peak Potentials for Potassium Arylmalononitrile Salts in CH₃CN and Their pK_{HA} in Me₂SO Using a Glassy Carbon and Platinum Disk Working Electrodes (*E*_{pa} in V, Relative to Ferrocene in CH₃CN)

subst	pK _{HA} ^a	glassy carbon <i>E</i> _{pa} vs. Ferrocene	platinum disk <i>E</i> _{pa} vs. E
NO ₂		+0.180	+0.309
Cl	3.14	-0.128	-0.013
H	4.24	-0.166	-0.073
CH ₃	4.85	-0.331	-0.127
OCH ₃	5.68	-0.374	

^aIn Me₂SO.

proaching equilibrium from the ions and in the presence of 1.31×10^{-2} m *n*-Bu₄N⁺BF₄⁻ as swamping electrolyte to yield a value of $K^{\circ}_{\text{het}} = 1.20 \pm 0.04 \times 10^{-4}$ from three determinations.^{8b} The agreement between equilibrium constants approached from either the ions or covalent crystals is within experimental error.

The validity of the Debye-Hückel limiting law for calculating mean activity coefficients for the (*p*-nitrophenyl)malononitrile and triphenylcyclopropenium ions in CH₃CN at 25 °C was confirmed for ionic strengths below 10⁻² m. *K*_{het} was determined at different ionic strengths by adding tetra-*n*-butylammonium tetrafluoroborate to 1.05 mM solutions of the covalent crystals in acetonitrile.

Solvent Effects. Standard free energies of heterolysis, $\Delta G^{\circ}_{\text{het}}$, were calculated from equilibrium constants in Table II by the expression $\Delta G^{\circ}_{\text{het}} = -RT \ln K^{\circ}_{\text{het}}$ and are presented there with the solvent dielectric constants.

The standard enthalpy of heterolysis for compound II, $\Delta H^{\circ}_{\text{het}}$, in acetonitrile was calculated from the temperature dependence of *K*_{het} by using the van't Hoff equation and equilibrium constants, both from reaction of the ions and from solution of the covalent crystals. The experimental values of $\Delta H^{\circ}_{\text{het}}$ are the same within experimental error: $\Delta H^{\circ}_{\text{het}} = 5.3 \pm 0.3$ kcal mol⁻¹ (as approached from the ions, *R* = 0.999) and $\Delta H^{\circ}_{\text{het}} = 5.4 \pm 0.5$ kcal mol⁻¹ (as approached from the covalent crystals, *R* = 0.999). The standard enthalpy of heterolysis was also determined in 1,2-dichloroethane as approached from the covalent crystals of compound II, giving a value of $\Delta H^{\circ}_{\text{het}} = 3.6 \pm 0.5$ kcal mol⁻¹ (*R* = 0.998).

Enthalpies of Carbocation-Carbanion Reactions by Calorimetry. Using calorimetry, the heats of reaction for a series of potassium arylmalononitriles reacting with trimethyl- and triphenylcyclopropenium tetrafluoroborate were measured in CH₃CN at 25 °C as described in the Experimental Section. The enthalpies of heterolysis of the covalent products are equivalent to the negative heats of reaction assuming that the enthalpy of ion pairing for KBF₄ is negligible. The results are shown in Table I. Values of $\Delta H^{\circ}_{\text{het}}$ in CH₃CN for (*p*-nitrophenyl)malononitrile reacting with triphenylcyclopropenium ion obtained by calorimetry ($\Delta H^{\circ}_{\text{het}} = 6.3 \pm 0.3$ kcal mol⁻¹) and the van't Hoff method ($\Delta H^{\circ}_{\text{het}} = 5.4 \pm 0.3$ kcal mol⁻¹) are in close agreement.

Cyclic Voltammetry. In all cases, the cyclic voltammograms exhibited irreversible behavior probably due to diffusion-controlled dimerization of the electrochemically generated radicals.

In Table III, the anodic peak potential values are reported relative to the potential of ferrocene for a series of potassium arylmalononitrile salts in acetonitrile along with their corresponding pK_{HA} values determined in Me₂SO by Bordwell.²⁶ The discrepancies between the peak potential values measured at the platinum disk and glassy carbon working electrodes are due to overpotentials.

The results show clearly that the energy required to oxidize the arylmalononitrile carbanions decreases steadily with increasing pK_{HA} (less stable carbanion).

The potentials for all carbocations studied were reported previously by Breslow²⁷ and by Volz.²⁸ Their results are summarized in Table IV. However, as a check, the cathodic peak potential value for tri-*p*-anisylmethyl tetrafluoroborate was measured in

Table IV. Published *E*_{1/2} Potentials for Carbocations

compound	<i>E</i> _{1/2} vs. SCE, V
tropylium tetrafluoroborate	-0.18 ^a and -0.17 ^b
triphenylcyclopropenium tetrafluoroborate	-0.72 ^a
trimethylcyclopropenium tetrafluoroborate	-1.16 ^a
tri- <i>p</i> -tolylmethyl perchlorate	+0.05 ^b
tri- <i>p</i> -anisylmethyl perchlorate	-0.07 ^a and -0.20 ^b
malachite green chloride	-0.64 ^b
crystal violet chloride	-0.79 ^b

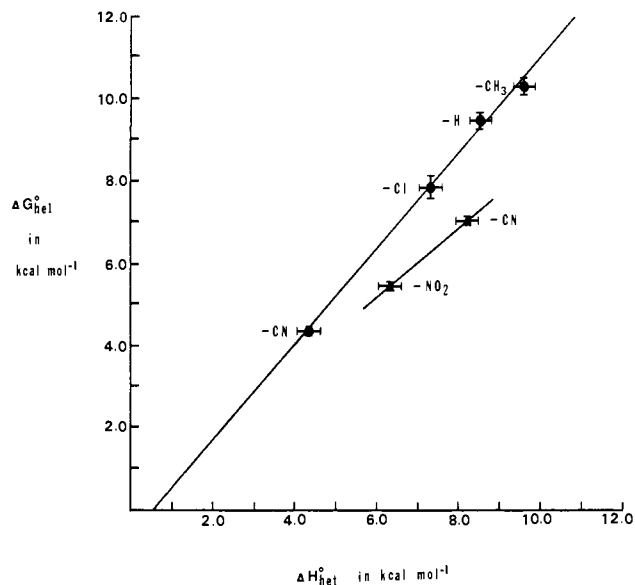
^aReference 27. ^bReference 28.

Figure 1. Comparison of the standard free energies of heterolysis with enthalpies of heterolysis for para-substituted phenylmalononitriletri- and triphenylcyclopropenes (●) (slope = 1.16; intercept = 0.66 kcal mol⁻¹; *R* = 0.998) and para-substituted phenylmalononitriletriphenylcyclopropenes (▲) in CH₃CN at 25.0 °C.

acetonitrile, *E*_{1/2} = -0.06, in agreement with the value *E*_{1/2} = -0.07 V reported by Breslow²⁷ but at variance with the -0.20 V reported by Volz.²⁸

Cyclic voltammograms for mixtures of (*p*-nitrophenyl)malononitrile anion and tri-*p*-anisylmethyl carbocation show peaks for both the carbanion and carbocation in acetonitrile solutions. Taken together, the voltammograms and ¹H NMR spectra of the ions in CD₃CN are consistent with the thermodynamic evidence that the covalent product exists in equilibrium with its ionic precursors.

Since reversible oxidation potentials could not be obtained for the arylmalononitrile carbanions, the standard free energies of electron transfer between the carbanions and carbocations could not be calculated reliably. However, the results do indicate that as the stabilities of arylmalononitrile anions and carbocations decrease, electron transfer becomes energetically more favorable. The cyclic voltammetry results are consistent with our product studies.

Discussion

The first goal of the research presented here was to find a system for which rates and equilibria for coordination/heterolysis reactions could be studied as a function of the structures of carbocation and carbanion, solvent, and temperature. This would permit for the first time an extensive examination of the relationship between the kinetics and thermodynamics of carbon-carbon bond formation and rupture in the absence of attacking or leaving nucleophiles.

The problem of finding carbocations and carbanions of sufficient stability to coexist in the same medium for a reasonable time turned out to be trivial. More serious potential obstacles were posed by the intrusion of charge-transfer⁶ and electron-transfer processes^{23,29} and ambident attack of carbanions on the rings of

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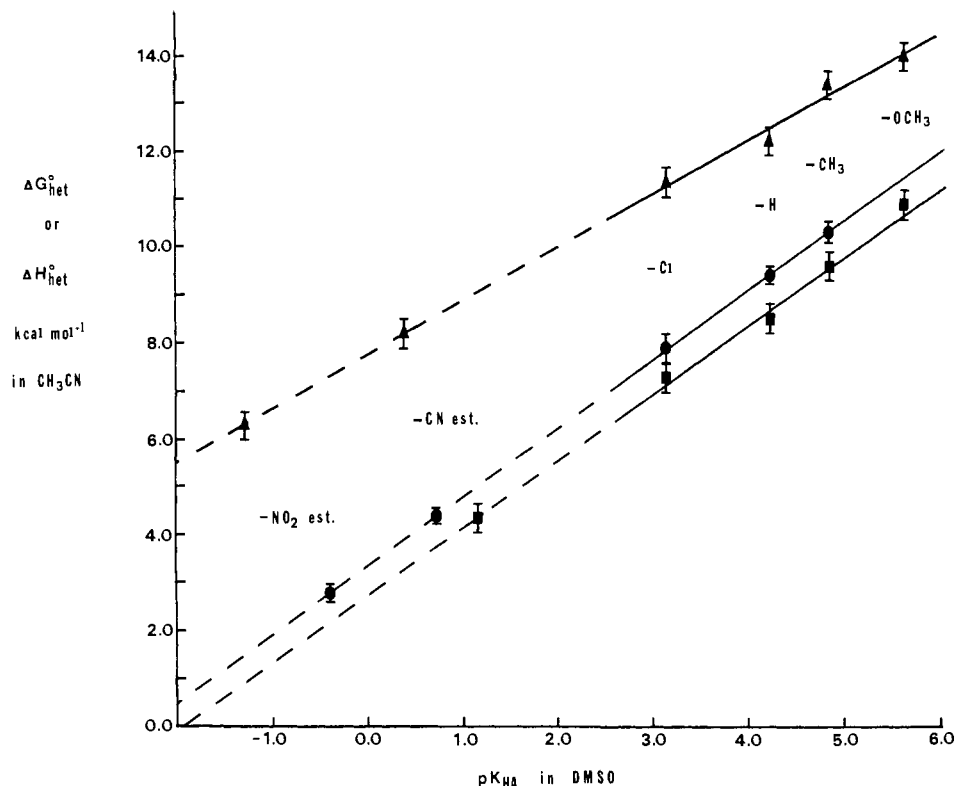


Figure 2. Comparison of the standard free energies of heterolysis and enthalpies of heterolysis of para-substituted phenylmalononitriletrimethylcyclopropenes and para-substituted phenylmalononitriletriphenylcyclopropenes with the pK_{HA} 's of the para-substituted phenylmalononitriles: \blacktriangle , enthalpies for para-substituted phenylmalononitriletriphenylcyclopropenes (slope = 1.11 kcal mol⁻¹; intercept = 7.74 kcal mol⁻¹; $R = 0.983$); \blacksquare , enthalpies for para-substituted phenylmalononitriletrimethylcyclopropenes (slope = 1.43 kcal mol⁻¹; intercept = 3.37 kcal mol⁻¹; $R = 0.999$); \bullet , free energies for para-substituted phenylmalononitriletrimethylcyclopropenes (slope = 1.41 kcal mol⁻¹; intercept = 2.76 kcal mol⁻¹; $R = 0.993$) [ΔG°_{het} and ΔH°_{het} in CH₃CN at 25.0 °C; pK_{HA} in Me₂SO at 25.0 °C].³³

triarylcarbonyl cations or the well-known tendency to photoheterolysis of compounds such as crystal violet cyanide.³⁰ Added to these problems, all of which are actually encountered at some point in this study, was the difficulty of retrieving and purifying from solution the covalent neutral products of carbocation-carbanion coordination. The weakness of the carbon-carbon bond (which was the chief focus of the study) prevented isolation of many otherwise promising covalent products. Although NMR spectra of such species seemed to be reasonably assigned in solution, it was important to obtain the structures of the covalent products if possible, from X-ray analysis of single crystals. After many failures with other combinations, the cyclopropenylarylmalononitriles and their ionic heterolysis products were arrived at as thoroughly feasible subjects for a systematic study.

Proof of Structure. Trimethylcyclopropenium ion and (*p*-nitrophenyl)malononitrile anion react cleanly to form a covalent product (I). Characterization of compound I by single-crystal X-ray analysis⁸ revealed an unusually long (1.58 Å) carbon-to-carbon bond between the cyclopropene ring and malononitrile carbons. Infrared and ¹H and ¹³C NMR spectra and elemental analysis were consistent with the single-crystal X-ray structure of compound I.

The related product II formed by the reaction of triphenylcyclopropenium ion with (*p*-nitrophenyl)malononitrile anion was characterized by the close analogy of its infrared, ¹³C NMR, and elemental analysis to compound I.

Although crystals of compounds I and II in diethyl ether gave colorless solutions, the orange color of the carbanion appeared readily in acetone or any more polar solvent. Both the ¹H and ¹³C NMR spectra of compound I in CDCl₃ at room temperature gave broad signals due to ionic-covalent equilibria. At -50 °C, the ¹H and ¹³C NMR spectra for compound I were resolved into signals corresponding to the covalent product. The ¹³C NMR

spectra of compound II in chloroform solution gave similar behavior. In addition, there is ample literature precedent for the heterolysis of triphenylcyclopropenium azide,³¹ trimethylcyclopropenium azide,²⁵ and tri-*tert*-butylcyclopropenium azide³² in solution as determined by ¹H NMR.

As might be expected, less stable carbanions such as (*p*-methylphenyl)malononitrile anion gave covalent products and did not exhibit time-averaged ¹³C NMR spectra in CDCl₃ solution at room temperature.

Room Temperature/Heterolysis. Equilibrium constants were determined by monitoring the arylmalononitrile anion absorbance. Identical values were obtained, within experimental error, by mixing solutions of the component ions or using solutions prepared from the pure covalent compound II.

No evidence of charge-transfer complexation or ion pair equilibria was detected by spectrophotometry since the spectra of equilibrium solutions were identical in shape to those of tetra-*n*-butylammonium (*p*-nitrophenyl)malononitrile salt solutions. Further thermodynamic support for a simple ionic-covalent equilibrium is suggested by the constant K°_{het} values measured at several concentrations, linear van't Hoff plots, and independent results from NMR and cyclic voltammetry.

The standard enthalpy of heterolysis for compound II was approached both from a solution of the covalent crystals and from a solution of the ionic salts through the temperature coefficient of K_{het} using the van't Hoff equation. Values of ΔH°_{het} were also determined directly by calorimetry by reaction of solutions of the ionic salts (potassium (*p*-nitrophenyl)malononitrile and triphenylcyclopropenium tetrafluoroborate). The slightly higher value obtained by the calorimetric method may be due to ion pairing of KBF₄, which would not affect the van't Hoff enthalpy values.

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The determination of the standard entropy of heterolysis for compound II, $\Delta S^\circ_{\text{het}}$, at 25 °C in acetonitrile by combination of $\Delta G^\circ_{\text{het}}$ and $\Delta H^\circ_{\text{het}}$ yields a value of $\Delta S^\circ_{\text{het}} = 3.05 \pm 2 \text{ cal mol}^{-1} \text{ deg}^{-1}$.

The positive value of $\Delta H^\circ_{\text{het}}$ is consistent with the endothermic breaking of a carbon-carbon bond. Also, the value of $\Delta S^\circ_{\text{het}}$ might be expected to be positive since the formation of two ions is the result of heterolysis. Apparently the solvation of the ions leads to an entropy loss that nearly compensates the gain in translational entropy. Since there must be a related exothermic enthalpy of solvation term, the enthalpy of heterolysis must be less endothermic than the actual value for rupturing the carbon-carbon bond. Thus, for compound II in acetonitrile the observed $\Delta G^\circ_{\text{het}} \approx \Delta H^\circ_{\text{het}}$. A more general correlation of $\Delta G^\circ_{\text{het}}$ vs. $\Delta H^\circ_{\text{het}}$ is given in Figure 1. The slopes of the correlation lines appear to depend on the size and presumably the electrostatic solvation entropy of the cation.

Table I and Figure 2 provide evidence for a direct relation between ion stability as measured by pK_{HA} and pK_{R^+} and the thermodynamic driving force for reaction of resonance-stabilized carbanions and carbocations to form covalent bonds.

Figure 2 relates both the free energies and the heats of reaction for a series of arylmalononitrile carbanions reacting with trimethyl- or triphenylcyclopropenium ion in acetonitrile to their corresponding pK_{HA} values determined in Me_2SO by Bordwell.³³ Unfortunately, values for the pK_{a} 's of the *p*- NO_2 and *p*- CN compounds were not available and so were estimated by extrapolation (dotted lines) and reading across from the measured $\Delta G^\circ_{\text{het}}$ or $\Delta H^\circ_{\text{het}}$. The slope of the line for measured points for compound II is $\Delta H^\circ_{\text{het}}/pK_{\text{HA}} = +1.11$ with a correlation coefficient of 0.98. Since the entropies of heterolysis are negligible for the compounds in Table I, a linear relationship should hold between the Brønsted and Lewis acidities for the series (i.e., $\Delta G^\circ_{\text{het}}$ vs. $\Delta G^\circ_{\text{i}}$). It is important to note, however, that heats of reaction used to derive $\Delta H^\circ_{\text{het}}$ were measured in acetonitrile but are being compared here to pK_{HA} measurements in Me_2SO . Unfortunately, the heats of reaction for this series could not be measured in Me_2SO because this solvent reacts slowly with cyclopropenium ions as determined by ^1H NMR. We hope that future studies will allow direct comparison of proton basicity with carbon basicity in the same solvent but for the moment consider that the difference between acetonitrile and Me_2SO is so small that the fundamental proportionality of the basicities of these resonance-stabilized anions against protonic acids and resonance-stabilized cations is established.

These results show that for a series of similar resonance-stabilized ions, the thermodynamics of proton transfer and carbocation transfer in solution are related closely. However, as Ritchie has shown recently³⁵ a general correlation for a wider variety of cations and anions cannot be expected.

Solvent Effects on the Free Energies of Heterolysis. Compounds I and II appear to be ideal for the investigation of electrostatic solvation on heterolysis equilibria. As shown in Figure 3, the free energies for heterolysis, $\Delta G^\circ_{\text{het}}$, are related linearly to the reciprocal of the solvent dielectric constant in accordance with the Born equation.³⁶

These solvents were selected carefully to reduce effects other than electrostatic solvation. Basic coordinating solvents like Me_2SO gave larger values for $\Delta G^\circ_{\text{het}}$ than expected from electrostatic solvation. Thus, heterolysis of compounds such as I and II appears to be an ideal model reaction for the separation of electrostatic and specific solvent effects such as basicity.

Comparison of Acetonitrile and 1,2-Dichloroethane. Thermodynamic properties for heterolysis of compound II have been measured in acetonitrile ($\Delta G^\circ_{\text{het}} = 5.39 \pm 0.03 \text{ kcal mol}^{-1}$, $\Delta H^\circ_{\text{het}} = 5.5 \pm 0.5 \text{ kcal mol}^{-1}$, $\Delta S^\circ_{\text{het}} = 0 \pm 2 \text{ cal K}^{-1} \text{ mol}^{-1}$) and

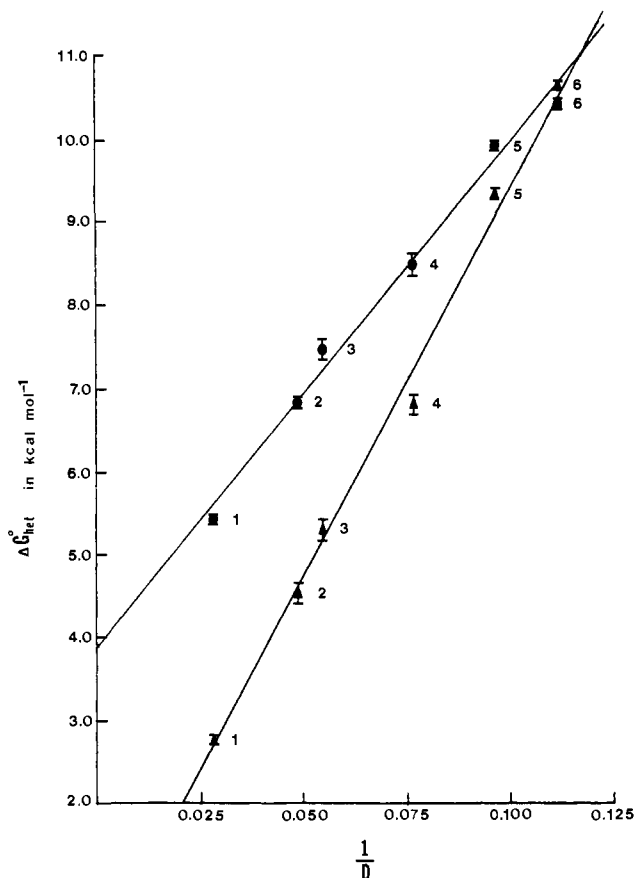


Figure 3. Born plot for the heterolysis of *p*-nitrophenylmalononitrile-triphenylcyclopropene (●) and *p*-nitrophenylmalononitrile-trimethylcyclopropene (▲) in several solvents at 25.0 °C: (1) acetonitrile, (2) acetone, (3) cyclohexanone, (4) 4-methyl-2-pentanone, (5) 1,2-dichloroethane, and (6) dichloromethane.

1,2-dichloroethane ($\Delta G^\circ_{\text{het}} = 9.91 \pm 0.03 \text{ kcal mol}^{-1}$, $\Delta H^\circ_{\text{het}} = 3.6 \pm 0.5 \text{ kcal mol}^{-1}$, $\Delta S^\circ_{\text{het}} = -21 \pm 2 \text{ cal K}^{-1} \text{ mol}^{-1}$). For comparison, Ritchie has reported the values for the heterolysis of crystal violet carbinol in water at 25 °C ($\Delta H^\circ_{\text{het}} = 6.6 \text{ kcal mol}^{-1}$ and $\Delta S^\circ_{\text{het}} = 0 \text{ cal K}^{-1} \text{ mol}^{-1}$).¹

Enthalpies and entropies for other ionization equilibria in polar and nonpolar media have been reported by Pearson.³⁷ Thermodynamic properties for heterolysis in acetonitrile and 1,2-dichloroethane are consistent also with the Born equation and its derivatives.³⁷ As the dielectric constant increases, the entropy of heterolysis should correspondingly become increasingly positive as observed for acetonitrile and 1,2-dichloroethane.

Electron-Transfer Studies. The fact that electron-transfer processes may compete with or even displace the more familiar nucleophilic/electrophilic two-electron processes has had great impact on mechanistic thinking during the past decade.^{29,39} The appearance of dimeric products from the anion in several carbocation-carbanion mixtures was a clear indication that electron transfer was probably an alternative channel for at least some coordination reactions.

In principle, the free energy required for electron transfer between carbanions and carbocations in homogeneous solution can be calculated by considering the electron-transfer reaction as two half-cell reactions if the free energy for homogeneous electron transfer in solution is equivalent to the calculated free energy for heterogeneous electron transfer at an electrode.⁴⁰

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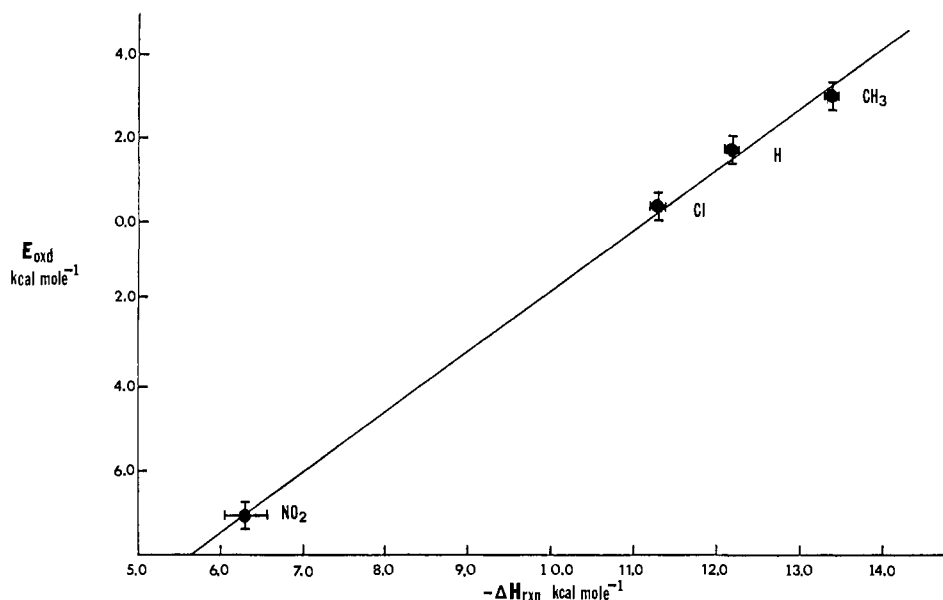


Figure 4. A comparison of the oxidation potentials for para-substituted arylmalononitrile carbanions to their heats of reaction with triphenylcyclopropenium tetrafluoroborate in CH_3CN at 25 °C.

The oxidation potentials for the arylmalononitrile salts, relative to the potential of ferrocene, were measured in acetonitrile at two working electrodes: platinum and glassy carbon, but the cyclic voltammograms for arylmalononitrile salts in acetonitrile indicated that electron transfer was irreversible at both electrodes. Table III compares the peak potentials of the anions at the glassy carbon and platinum disk electrodes with each other in acetonitrile and with the $\text{p}K_{\text{HA}}$'s of their conjugate acids in Me_2SO . Although the peak potential on glassy carbon is always more negative than on platinum, the difference varies considerably. Yet it is clear that these crude estimates of the redox potential of the anions follow the same trend as their basicities.

Federlin and co-workers⁴¹ have observed a good linear free energy relationship over 25 $\text{p}K_{\text{HA}}$ units (from 6 to 30) for a variety of carbanions in Me_2SO , including phenylacetone nitriles, with a slope of 1.13 $\Delta V/\Delta G^\circ$, (expressed in kcal mol^{-1}). Thus, for a series of structurally similar carbanions, the likelihood of electron transfer to carbocations increases in proportion to their basicities. In view of the many qualifications regarding the four anions in Table III for which we have both peak potentials and $\text{p}K_{\text{HA}}$'s, we believe it would be misleading to estimate a quantitative relationship for this series.

The results of Breslow²⁷ and Volz²⁸ indicate that carbocations are reduced more easily as their stabilities ($\text{p}K_{\text{R}^+}$) decrease for a series of triarylmethyl carbocations. Reduction potentials for carbocations vary from 0.05 V for tri-*p*-tolylmethyl carbocation to -1.3 V for trimethyl cyclopropenium ion corresponding to an energy difference of $\sim 31 \text{ kcal mol}^{-1}$. Therefore, tri-*p*-tolylmethyl carbocation might be expected to react more easily by an electron-transfer pathway than trimethylcyclopropenium ion.

Although the direct calculation of the free energy for electron transfer between carbocations and carbanions was not feasible, the relative redox potentials of carbocations and carbanions were consistent with product studies. Stable carbocations (e.g., crystal violet and cyclopropenium ions), which are also difficult to reduce, do not give dimerization products on reaction with carbanions. Less stable carbocations such as tri-*p*-tolylmethyl carbocation ($\text{p}K_{\text{R}^+} = -3.56$, $E_{\text{red}} = +0.05 \text{ V}$)⁴¹ and tri-*p*-anisylmethyl carbocation ($\text{p}K_{\text{R}^+} = +0.82$, $E_{\text{red}} = -0.07 \text{ V}$)⁴² which are more easily reduced, reacted with (*p*-methylphenyl)malononitrile ($\text{p}K_{\text{HA}} = 4.85$, $E_{\text{ox}} = -0.33 \text{ V}$)⁴³ and (*p*-nitrophenyl)malononitrile ($E_{\text{ox}} = +0.18 \text{ V}$)⁴³ carbanions to give dimerization products.

For carbanions, the enolate anions are the most difficult to oxidize and gave no dimerization products on reaction with carbocations. Of the arylmalononitrile salts, (*p*-methylphenyl)malononitrile reacts with tropylium ion to yield dimerization products while (*p*-nitrophenyl)malononitrile reacts by coordination.

In Figure 4, the observed peak potentials at the platinum electrode from Table III have been treated as relative free energies for electron transfer in acetonitrile (despite the shortcomings described above) and are plotted against the enthalpies of reaction for a series of arylmalononitrile carbanions reacting with triphenylcyclopropenium tetrafluoroborate in acetonitrile. As mentioned previously, the standard free energy of heterolysis for compound II is nearly equivalent to the enthalpy of heterolysis in acetonitrile. If this relationship is approximated for other arylmalononitriles and the true reversible redox potentials are close to the peak potentials in Table III, the expected proportionality between electron transfer and free energy of reaction is found with the former somewhat more sensitive to substituent changes than the latter. Bordwell has indicated that the kinetics of electron-transfer reactions are approximately three times more sensitive to Brønsted basicity than are nucleophilic substitution reactions⁴⁴ while Russell⁴⁵ and Zeigler⁴⁶ have found that less stable carbanions (e.g., benzyl carbanion) and benzyl halides react by electron transfer instead of the simple coordination channel.

Solvent Effects on Redox Potentials. The fact that simple coordination of (*p*-nitrophenyl)malononitrile anion with trianisylmethyl carbocation occurs in acetone or acetonitrile while electron transfer occurs in ligroine-methylene chloride mixtures implied that solvent effects may play an important role in electron-transfer reactions between carbanions and carbocations^{47,48} so that competition between polar and free radical pathways might be controlled by suitable choice of medium.

Conclusions

By careful consideration of $\text{p}K_{\text{HA}}$, $\text{p}K_{\text{R}^+}$, and redox potentials of resonance-stabilized carbocations and carbanions, covalent compounds I and II were designed that exist in equilibria with their carbanion and carbocation precursors in solution. Com-

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pounds I and II are (to our knowledge) novel since they contain carbon-to-carbon bonds that cleave by merely dissolving them in solution.

The thermodynamics of carbon-carbon bond formation is related closely to the pK_{HA} and pK_{R^+} of the carbanion and carbocation. For para-substituted arylmalononitrile carbanions reacting with substituted cyclopropenium ions the Brønsted basicity of the carbanions was related linearly to their basicities toward the carbocations (e.g., Lewis basicities). The apparent (irreversible) oxidation potentials were also proportional to the Lewis basicities of the anions toward the triphenylcyclopropenium ion.

Preliminary kinetic studies⁸ indicate that carbanion-carbocation reactions are affected by the stabilities and ion pairing of the carbanions and carbocations. The relation between kinetics and thermodynamics will be a primary area for our future research.

The effect of solvent on the heterolytic equilibria of compounds I and II follows the Born equation and the Debye-Hückel limiting law and provides a starting point for a more extensive investigation of the solvation of less stable carbocations and carbanions.

Some carbanions and carbocations reacted by electron transfer in a pattern related to their redox potentials. Electron transfer appeared to be more sensitive to substituent variation than was coordination. Thus, the likelihood of electron transfer instead of simple coordination increases as the stability of the carbocation and carbanion decreases. Since both reactions are highly sensitive to solvent polarity, it may be possible to control the competition between bond formation by coordination vs. electron transfer through suitable choice of medium.

Acknowledgment. We are pleased to acknowledge support for this work from NSF Grant CHE-8006202 the assistance of Professors C. W. Anderson and A. T. McPhail and helpful suggestions by Professor C. D. Ritchie.

Registry No. $\text{CH}_3\text{CH}_2\text{CH}(\text{C}(\text{O})\text{OMe})_2$, 26717-67-9; $\text{CH}_3\text{CH}_2\text{CH}(\text{C}(\text{O}_2\text{H})_2)$, 601-75-2; $\text{CH}_3\text{CH}(\text{C}(\text{O})\text{OMe})_2$, 609-02-9; $\text{CH}_3\text{CH}(\text{CO}_2\text{H})_2$,

516-05-2; $\text{CH}_3\text{C}(\text{O})\text{CH}_3$, 67-64-1; $\text{CH}_3\text{C}(\text{O})(\text{CH}_3)\text{HC}(\text{O})\text{CH}_3$, 815-57-6; $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{C}(\text{O})\text{CH}_3$, 123-54-6; $\text{CH}_3\text{C}(\text{O})\text{C}(\text{Et})\text{HC}(\text{O})\text{CH}_3$, 1540-34-7; $\text{HO}_2\text{CCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{CO}_2\text{H}$, 4839-46-7; $\text{CH}_3(\text{CH}_2)_2\text{C}(\text{O})\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{C}(\text{O})\text{OEt}$, 91879-91-3; *p*- $\text{NO}_2\text{C}_6\text{H}_4\text{CH}(\text{CN})_2$, 7077-65-8; *p*- $\text{NO}_2\text{C}_6\text{H}_4\text{CH}_2\text{CN}$, 555-21-5; *p*- $\text{ClC}_6\text{H}_4\text{CH}(\text{CN})_2$, 32122-64-8; *p*- $\text{ClC}_6\text{H}_4\text{CH}_2\text{CN}$, 140-53-4; *p*- $\text{ClC}_6\text{H}_4\text{CHCN}^-\text{Na}^+$, 60389-37-9; PhOCN , 1122-85-6; *p*- $\text{CNC}_6\text{H}_4\text{CH}(\text{CN})_2$, 91879-92-4; *p*- $\text{MeC}_6\text{H}_4\text{CH}(\text{CN})_2$, 33534-88-2; *p*- $\text{MeOC}_6\text{H}_4\text{CH}(\text{CN})_2$, 33534-87-1; $\text{PhCH}(\text{CN})_2$, 3041-40-5; PhOH , 108-95-2; *p*- $\text{CNC}_6\text{H}_4\text{C}(\text{CN})_2^-$, 91880-06-7; *p*- $\text{CNC}_6\text{H}_4\text{C}(\text{CN})_2^- \text{K}^+$, 91879-93-5; *p*- $\text{ClC}_6\text{H}_4\text{C}(\text{CN})_2^-$, 91880-07-8; *p*- $\text{ClC}_6\text{H}_4\text{C}(\text{CN})_2^- \text{K}^+$, 87658-34-2; *p*- $\text{MeC}_6\text{H}_4\text{C}(\text{CN})_2^-$, 91880-08-9; *p*- $\text{MeC}_6\text{H}_4\text{C}(\text{CN})_2^- \text{K}^+$, 87658-35-3; *p*- $\text{MeC}_6\text{H}_4\text{C}(\text{CN})_2\text{CH}_3$, 91879-94-6; *p*- $\text{MeOC}_6\text{H}_4\text{C}(\text{CN})_2^-$, 85535-17-7; *p*- $\text{MeOC}_6\text{H}_4\text{C}(\text{CN})_2^- \text{K}^+$, 91879-95-7; $\text{PhC}(\text{CN})_2^-$, 45884-26-2; $\text{PhC}(\text{CN})_2^- \text{K}^+$, 91879-96-8; *p*- $\text{NO}_2\text{C}_6\text{H}_4\text{C}(\text{CN})_2^-$, 56577-73-2; *p*- $\text{NO}_2\text{C}_6\text{H}_4\text{C}(\text{CN})_2^- \text{K}^+$, 20394-72-3; *p*- $\text{NO}_2\text{C}_6\text{H}_4\text{C}(\text{CN})_2^- \text{Bu}_4\text{N}^+$, 91879-97-9; Bu_4NOH , 2052-49-5; (*p*- MeC_6H_4)₃ COH , 3247-00-5; *p*- $\text{MeC}_6\text{H}_4\text{MgBr}$, 4294-57-9; *p*- $\text{MeC}_6\text{H}_4\text{C}(\text{O})\text{OMe}$, 99-75-2; (*p*- MeC_6H_4)₃ C^+BF_4^- , 1650-48-2; (*p*- MeOC_6H_4)₃ COH , 3010-81-9; *p*- $\text{MeOC}_6\text{H}_4\text{MgBr}$, 13139-86-1; *p*- $\text{MeOC}_6\text{H}_4\text{C}(\text{O})\text{OMe}$, 121-98-2; (*p*- MeOC_6H_4)₃ C^+BF_4^- , 437-30-9; $(\text{CH}_3)_3\text{CC}(\text{O})\text{C}[(p\text{-MeC}_6\text{H}_4)_3\text{C}]\text{HC}(\text{O})\text{C}(\text{CH}_3)_3$, 19672-57-2; dime-done, 126-81-8; 2-methyldimedone, 1125-11-7; 2-ethylimedone, 2406-29-3; methyl Meldrum's acid, 3709-18-0; ethyl Meldrum's acid, 17216-65-8; *p*- $\text{NO}_2\text{C}_6\text{H}_4\text{C}(\text{CN})_2\text{C}(\text{CN})_2\text{C}_6\text{H}_4$ -*p*- NO_2 , 7061-41-8; triphenylcyclopropene, 16510-49-9; triphenylcyclopropenyl, 12190-17-9; triphenylcyclopropenyl tetrafluoroborate, 741-16-2; trimethylcyclopropenyl, 26827-04-3; trimethylcyclopropenyl tetrafluoroborate, 30109-53-6; tropylium tetrafluoroborate, 27081-10-3; (1,2,3-triphenylcyclopropenyl)(*p*-nitrophenyl)malononitrile, 86943-83-1; (1,2,3-triphenylcyclopropenyl)(*p*-cyanophenyl)malononitrile, 91879-98-0; (1,2,3-triphenylcyclopropenyl)(*p*-methylphenyl)malononitrile, 91879-99-1; (1,2,3-trimethylcyclopropenyl)(*p*-nitrophenyl)malononitrile, 86943-82-0; (1,2,3-trimethylcyclopropenyl)(*p*-chlorophenyl)malononitrile, 91880-00-1; (1,2,3-trimethylcyclopropenyl)(*p*-cyanophenyl)malononitrile, 91880-01-2; (1,2,3-trimethylcyclopropenyl)(*p*-methylphenyl)malononitrile, 91880-02-3; (1,2,3-trimethylcyclopropenyl)(*p*-methoxyphenyl)malononitrile, 91880-03-4; (1,2,3-trimethylcyclopropenyl)phenylmalononitrile, 91880-04-5; 4-tropyl-2,2,6,6-tetramethyl-3,5-heptanedione, 91880-05-6; cyanogen chloride, 506-77-4.

Novel Bicycloannulation via Tandem Vinylation and Intramolecular Diels-Alder Reaction of Five-Membered Heterocycles: A New Approach to Construction of Psoralen and Azapsoralen

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Received March 19, 1984

Abstract: *trans*-4-(Phenylsulfinyl)-3-buten-2-one (**1**) was found to undergo a new versatile addition-elimination reaction with five-membered compounds such as furans, pyrroles, imidazole, pyrazole, and 6-(dimethylamino)fulvene to give an excellent yield of the corresponding *trans*-4-aryl-3-buten-2-ones (**3**). The thermal reaction of the propargyl ethers **7a,b** prepared from **3a,b** gave a single intramolecular Diels-Alder adduct, **8a,b**, in 59% and 38% yields, respectively. Treatment of **7a,b** with *t*-BuOK in refluxing *tert*-butyl alcohol afforded another type of Diels-Alder adduct, **10a,b**, in almost quantitative yields. This bicycloannulation strategy was applied to a new synthesis of psoralen which is of current interest due to its unique photoreactivity with DNA. The acid-catalyzed reaction of sulfoxide **12**, prepared from ethyl acetoacetate in high yield, with furan gave **13** in 78% yield. The intramolecular Diels-Alder reaction of the neopentyl acetal of **13** in the presence of Pd/C followed by acid hydrolysis afforded the tricyclic ketone **18** in 38% yield. Baeyer-Villiger oxidation and dehydrogenation of **18** completed the synthesis of psoralen (**11**). Furthermore, hitherto unknown azapsoralen **20** was also synthesized by this method.

The widespread occurrence of linearly fused heterocyclic [5.6.*n*] ring systems in natural products stimulates the development of new strategies.¹ A potentially very versatile approach envisions

an intramolecular Diels-Alder reaction² of heterocyclic aromatic compounds possessing a 2-vinyl substituent (i.e., A) and a subsequent aromatization to give B as outlined in eq 1. The key to