Synthesis and Reactions of Highly Electrophilic Imines Containing the N-Cyano Group

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Toluene solutions of tricyanomethanimine, 1, and methyl 3-aza-2,3-dicyanoacrylate, 2, were synthesized by thermal decomposition of, respectively, 2,2-diazido-1,1-dicyanoethylene and methyl 3,3-diazido-2-cyanoacrylate. Diethyl (cyanoimino)malonate, 3, was obtained from the reaction of diethyl ketomalonate with bis(trimethylsilyl)carbodiimide. None of these electrophilic imines could be isolated, because oligomerization occurred in every case. Dilute solutions of 1 and 2 in toluene were stable for several days, so the imines were characterized in solution. Cycloaddition reactions with 2,3-dimethylbutadiene and cyclopentadiene lead to the expected Diels–Alder adducts. With p-methoxystyrene, spontaneous copolymerizations occurred with both 1 and 2. These imines were somewhat less electrophilic than tetracyanoethylene; they behave similarly in cycloaddition reactions, but in contrast they are also able to polymerize.

Introduction

In organic monomer chemistry, C=C and C=O compounds, i.e. vinyl derivatives and aldehydes, have been extensively investigated, but C=N monomers are almost unknown. We started a systematic investigation of the polymerizability of the C=N monomers with a study of 1-aza-1,3-butadienes[1] and 2-aza-1,3-butadienes[2] carrying aryl substituents at the 1-position for possible polymerization through the C=N bonds. The participation of the C=N bond (4,1-polymerization) in the polymerization of these monomers was higher than achieved in earlier literature,[3,4] but these monomers still underwent substantial C=C bond opening. Stabilization of the growing species by aryl was not sufficient to polymerize exclusively through the azabutadiene function. More recently, we studied N-carbethoxy-3-methyl-1-aza-1,3-butadiene.[5] The presence of an electron-withdrawing substituent on nitrogen led to efficient anionic polymerization in 4,1-fashion. In the presence of free-radical initiators, hetero-Diels–Alder dimerization competed with polymerization, and only low conversion to polymers with mixed structures was obtained.

As to compounds containing only the C=N group, an earlier study in this laboratory had shown that diethyl (carbethoxyimino)malonate,[6] a moderately electrophilic imine, gives only hetero-Diels–Alder cycloadditions involving the N-COOEt group, and no polymerization, in agreement with the results obtained for the N-carbethoxyazabutadiene derivative. Azaethylenes with N-cyano substituents would be free of this complication. 2-Phenyl-N-cyanoazaethylene and 2-tert-butyl-N-cyanoazaethylene were investigated.[7] The former led to oligomers under anionic polymerization conditions.

In this paper, we investigate the synthesis, cycloaddition, and polymerizability of several very highly electrophilic imines containing CN groups on nitrogen. The compounds selected were tricyanomethanimine, 1, methyl 3-aza-2,3-dicyanoacrylate, 2, and diethyl (cyanoimino)malonate, 3. The synthesis and properties of 1 have been described in a preliminary report.[8]
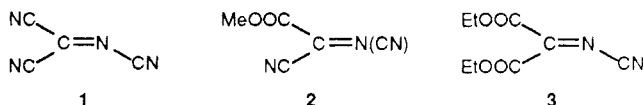

Results

Monomer Syntheses. Many conventional attempts to synthesize these N-cyano-substituted methanimines failed,

perhaps accounting for their absence from the literature: retro-Diels–Alder reaction of the cyclopentadiene adduct of the desired imines or dehydrogenation of the saturated amine equivalent, for example, did not lead to the target compounds. Finally, we found a clue in the work of Saalfrank and co-workers:[9] decomposition of methyl 3,3-diazido-2-cyanoacrylate (4) in methanol at 60 °C led in good yield to methyl 3-aza-3-cyano-2-methoxyacrylate, 5. The authors proposed the following mechanism:
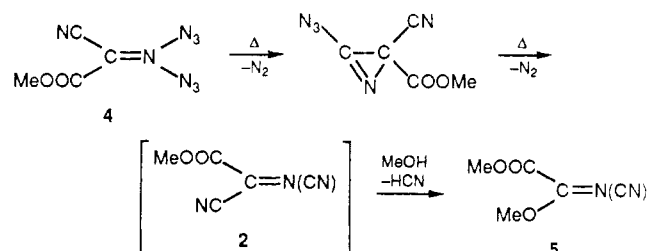
Similar reactions and mechanisms have been reported in the literature.[10,11] The intermediate 2 could be trapped as the Diels–Alder adduct if the reaction was run in the presence of 2,3-dimethylbutadiene. We hoped that if the reactions were run in a nonnucleophilic solvent, the reaction could be stopped at the methanimine stage.

For the synthesis of tricyanomethanimine, 1, the starting material 2,2-diazido-1,1-dicyanoethylene (7) was obtained from 2,2-dichloro-1,1-dicyanoethylene (6).[12,13] The diazide 7 did not solidify; the IR spectrum showed the expected
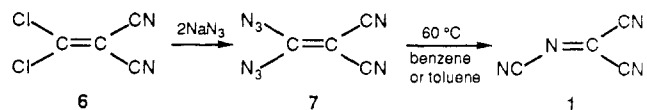
(1) Kitayama, T.; Hall, H. K., Jr. *Macromolecules* **1987**, *20*, 1451.
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(3) Sato, H.; Tsuruta, T. *J. Macromol. Sci.-Chem.* **1970**, *A4*, 295.
(4) Smith, W.; Norton, D. G.; Ballard, S. A. *J. Am. Chem. Soc.* **1953**, *75*, 3316.
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(6) Hall, H. K., Jr.; Miniutti, D. L. *Tetrahedron Lett.* **1984**, *25*, 943.
(7) Kim, J. B.; Padias, A. B.; Hall, H. K., Jr. *Macromolecules* **1990**, *23*, 21.
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(9) Saalfrank, R. W.; Ackermann, E.; Fischer, M.; Wirth, U. *Chem. Ber.* **1987**, *120*, 2003.
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(12) Josey, A. D.; Dickinson, C. L.; Dewhirst, K. C.; McKusick, B. C. *J. Org. Chem.* **1967**, *32*, 1941.
(13) Carrie, R.; Daniom, D.; Ackerman, E.; Saalfrank, R. W. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 287.

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2160 cm⁻¹ absorption. This procedure was only run in small amounts (1-g scale), because the diazide is highly explosive (DANGER!). Addition of the diazide **7** to benzene or toluene at 60 °C resulted in the formation of the desired compound **1**. Tricyanomethanimine (**1**) could not be isolated, but was completely characterized by IR, mass, and ¹³C NMR spectroscopy in solution. Tricyanomethanimine (**1**) was stable as a dilute solution and could be stored in toluene at –50 °C for long periods (several days). However, concentration of the solution always resulted in oligomerization. Addition of radical inhibitor or traces of acid did not prevent oligomerization.

Replacing one cyano substituent by an ester function should lower the electrophilic character of **1** and hopefully increase the stability. Therefore, methyl 3,3-diazido-2-cyanoacrylate (**4**) was synthesized from methyl 3,3-dichloro-2-cyanoacrylate (**8**) according to literature procedures.[14,15] Diazide **4** is a white solid and also an explosive (DANGER!). By performing the thermal decomposition of **4** in benzene or toluene, the desired methyl 3-aza-2,3-dicyanoacrylate, **2**, was indeed obtained in solution.
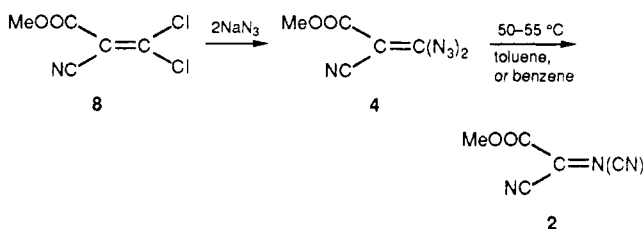
Unfortunately **2** could not be isolated either, as oligomerization occurred as soon as the solvent was removed. Imine **2** was again fully characterized in solution: IR, MS, and ¹H and ¹³C NMR. Both ¹H and ¹³C NMR spectra indicate the presence of both possible isomers. When methanol was added to a toluene solution of **2**, the color disappears immediately and the NMR spectrum confirms the formation of methyl 3-aza-3-cyano-2-methoxyacrylate (**5**) in agreement with Saalfrank's data.[9]

Because **2** was still not isolable, we tried to synthesize *N*-cyanomethanimines with two ester functionalities. Efforts toward the synthesis of dimethyl (diazidomethylene)malonate from dimethyl (dichloromethylene)-malonate[14,15] failed, because of insufficient reactivity. Therefore, an alternate synthesis route was investigated. In the synthesis of 2-phenyl-*N*-cyanoazaethylene, benzaldehyde was reacted with bis(trimethylsilyl)carbodiimide in the presence of titanium tetrachloride.[7] Accordingly, the commercially available diethyl ketomalonate was mixed with bis(trimethylsilyl)carbodiimide and a catalytic amount of TiCl₄. The infrared spectrum of the dilute solution indicates the presence of C=N bonds, but here again, attempted isolation led to oligomerization.
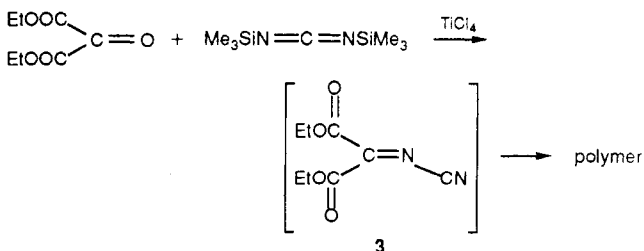
Electrophilic Character. Cyclic voltammetry of a 5 × 10⁻⁴ M benzene solution of **1** showed an irreversible

Table I. AM1 Molecular Orbital Calculation

|	*E* HOMO, eV	*E* LUMO, eV	heat of formation, kcal/mol
(NC)₂C=C(CN)₂	–11.52	–2.52	152.38
NC, NC / C=N \ CN	–12.32	–2.19	135.2
NC, H₃COOC / C=N \ CN	–11.86	–2.02	21.17
H₃COOC, NC / C=N \ CN	–11.36	–1.71	–0.8
(H₃COOC)₂C=N \ CN	–11.58	–1.56	–94.71

reduction peak at –0.16 V in 0.1 M tetrabutylammonium tetrafluoroborate in dichloromethane using Ag/0.1 M AgNO₃ in acetonitrile as a reference electrode and a scan rate of 100 mV/s. For comparison under the same conditions, TCNE showed a reversible peak at –0.11 V.

AM1 calculations[16] were performed for the electrophilic imines under study. The data are summarized in Table I. From the energy levels of the LUMO, we can conclude that tricyanomethanimine **1** (–2.19 eV) is almost as electrophilic as tetracyanoethylene (TCNE) (–2.52 eV); this is in agreement with the cyclic voltammetry data. For the monoester derivative **2**, the *Z* isomer (–2.02 eV) is calculated to be more electrophilic than the *E* isomer (–1.71 eV), and as expected, dimethyl (cyanoimino)malonate (–1.56 eV) is the least electrophilic.

Reactions. Cycloaddition of solutions of **1** or **2** with 2,3-dimethyl-1,3-butadiene or cyclopentadiene afforded the corresponding Diels–Alder adducts as crystalline solids, which were characterized by ¹H NMR and elemental analyses. The two isomers of **12** (endo and exo) were obtained, but they could not be separated.
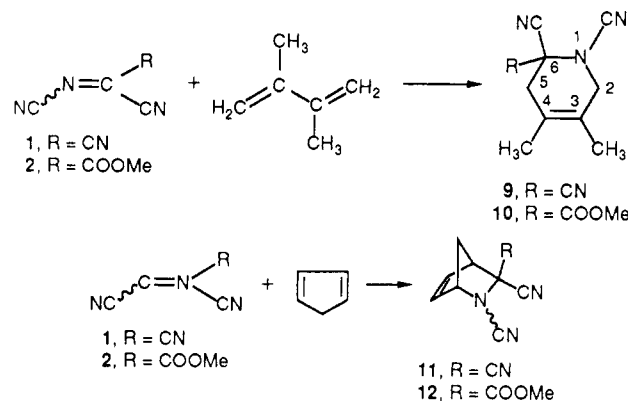
The cyclopentadiene adduct **11** was identical to material obtained via a different route in an earlier study.[17] In that case 2,2-dicyanomethanimine tosylate was reacted with cyclopentadiene, and the tosylate group was transformed to an *N*-cyano substituent via the urea.
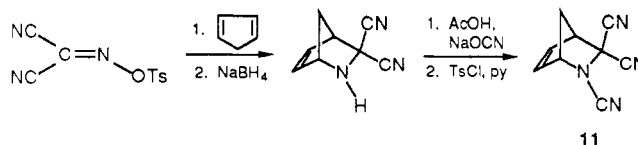
Pyrolysis of the cycloadducts **11** and **12** at 750 °C and 0.1 mmHg did not result in formation of the original imines

(14) Gompper, R.; Topel, W. *Chem. Ber.* **1962**, *95*, 2861.
(15) Gompper, R.; Kunz, R. *Chem. Ber.* **1962**, *99*, 2900.

(16) Dewar, M. J. S.; Starch, D. M. *J. Am. Chem. Soc.* **1985**, 3898.
(17) Flury, P.; Hall, H. K., Jr., unpublished results.

1 and 2, and only polymeric materials and starting materials were obtained.

Attempted cycloaddition reactions of the dilute solution of diethyl (cyanoimino)malonate (3) with 2,3-dimethylbutadiene always resulted in polymerization of the diene. The catalytic amount of titanium tetrachloride was still present in the solution and initiated the cationic polymerization of the butadiene. Therefore, the cycloadditions of 3 could not be studied under these conditions.

Deeply colored charged-transfer complexes were obtained from the reaction of 1 with moderately electron-rich compounds such as anisole or hexamethylbenzene. The more electron-rich *N,N*-dimethylaniline underwent electrophilic aromatic substitution[18] to yield 13. Therefore,
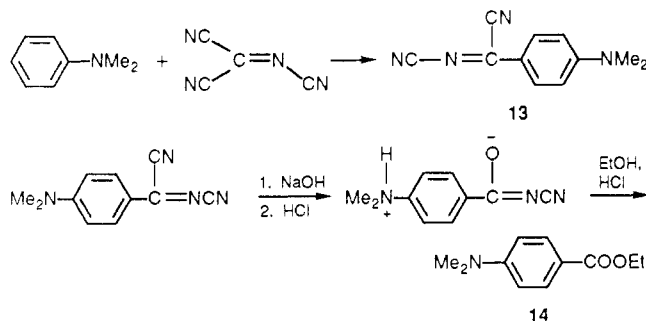

the reaction product was hydrolyzed, and the hydrolysis product ethyl *p*-(dimethylamino)benzoate (14) indicated that the aromatic substitution occurred at the C-position of the imine.

The reaction of 2 with *N,N*-dimethylaniline only resulted in the formation of a colored solution of the charge-transfer complex. This is an indication of the greater reactivity of 1 over 2 in the electrophilic aromatic substitution reaction.

Polymerizations. The electrophilic imines 1 and 2 oligomerized spontaneously upon attempted isolation. These oligomers are completely insoluble and can only be characterized by IR spectroscopy and chemical analysis. They are yellow powders which do not melt but decompose above 120 °C.

Spontaneous copolymerization of 1 and 2 with *p*-methoxystyrene successfully produced copolymers. Based on NMR data and chemical analysis, an alternating structure is proposed for these polymers. Copolymer 15 was soluble
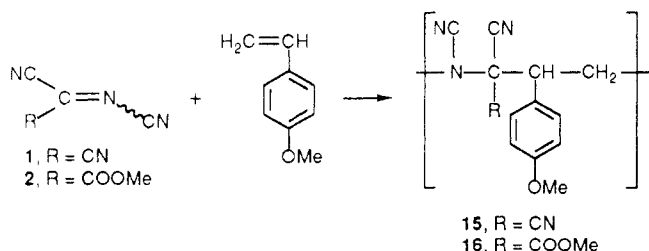
in chloroform. The backbone methylene protons are observed at 3.7 ppm in the NMR spectra, confirming the structure of the polymer as shown. Size-exclusion chromatography revealed very broad molecular weight distribution with a maximum at about 2000 versus polystyrene standards. Copolymer 16 was insoluble in chloroform but soluble in DMSO; the NMR confirms structure 16.

An equimolar mixture of 1 and styrene did not result in copolymer. The reaction was run both with and without

radical initiator; homopolymer of 1 was the only product in both instances.

Discussion

Conventional synthesis methods, such as Schiff base reactions or retro Diels–Alder reactions, were not useful for the synthesis of the highly electrophilic imines in this study. Thermal decomposition of 2,2-diazidoethylenes yielded the desired *N*-cyano-substituted imines 1 and 2. The formation of these 2,2-diazidoethylenes is a nucleophilic substitution reaction by sodium azide on an activated 2,2-dichloroethylene. The solvent is highly polar, namely aqueous acetone. The substitution using sodium azide is only possible if there is at least one cyano substituent on the double bond, as shown by the synthesis of 4 and 7. The substitution does not proceed with two ester groups on the β-carbon. Therefore, an alternative method was necessary to synthesize a (cyanoimino)malonate. The synthesis using bis(trimethylsilyl)carbodiimide, and titanium tetrachloride was successful, as shown by the IR spectrum, but the product 3 could not be isolated and the presence of TiCl₄ interfered with further reactions.

None of the *N*-cyanomethanimines synthesized in this study could be isolated. They all oligomerized when the solvent was removed, even in the presence of radical inhibitors or acid (inhibitor for anionic polymerization). This instability could be due to the high electrophilic character of these compounds, which makes them very susceptible to anionic and/or free-radical polymerization.

The [4 + 2] cycloadditions of 1 and 2 with 2,3-dimethylbutadiene and cyclopentadiene follow the expected behavior for an electrophilic dienophile. With *p*-methoxystyrene, however, the radical copolymerization proceeds spontaneously. The initiation can be explained in terms of our Bond-forming Initiation theory,[19] in which a tetramethylene intermediate is proposed to be the initiator. In this case, we hypothesize that the initiation proceeds in the following way:
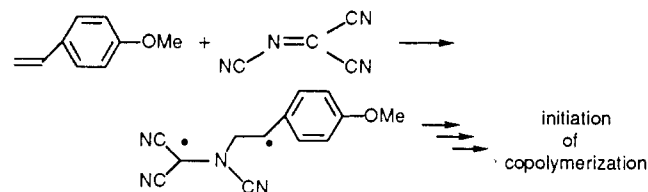
If we compare the behavior of the electrophilic imines 1 and 2 with TCNE, a standard electrophilic olefin, we can conclude the following: (1) 1 and 2 are somewhat less electrophilic than TCNE, as shown by the AM1 calculations, the cyclic voltammetry and by a rough comparison of the cycloaddition rates with electron-rich dienes. (2) TCNE is stable at room temperature, while the electrophilic imines are only stable in dilute solutions. (3) With *p*-methoxystyrene, TCNE readily forms the cyclobutane adduct via a zwitterionic tetramethylene intermediate. Both electrophilic imines 1 and 2 copolymerize spontaneously with *p*-methoxystyrene. (4) TCNE does not polymerize. Both imines 1 and 2 spontaneously homopolymerize and copolymerize with *p*-methoxystyrene. The nature of the homopolymerization is not clear, as neither free-radical or anionic inhibitors had any effect.

Experimental Section

Instrumentation. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker WM-250 NMR spectrometer at 250 MHz.

(18) McKusick, B. C.; Heckert, R. E.; Cairns, T. L.; Coffman, D. D.; Mower, H. F. *J. Am. Chem. Soc.* **1957**, *80*, 2806.

(19) Hall, H. K., Jr. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 440.

Infrared spectra were recorded on a Perkin-Elmer Model 983 infrared spectrophotometer. Melting points were determined on a Hoover capillary melting point apparatus and are uncorrected. Mass spectra were determined on a Hewlett-Packard Model 5988A, RTE-6/vM Data System Direct Insertion Probe. Elemental analyses were performed by Desert Analytics, Tucson, AZ.

Reagents. 2,2-Dichloro-1,1-dicyanoethylene (6) and methyl 3,3-dichloro-2-cyanoacrylate (8) were prepared according to literature procedures.[12,14] Diethyl ketomalonate was obtained from Aldrich and used without purification. Bis(trimethylsilyl)-carbodiimide was prepared according to a literature procedure.[20]

Tricyanomethanimine (1). A solution of 1,1-dichloro-2,2-dicyanoethylene (6.7 mmol, 1 g), 6, in a acetone (5 mL) was added at -20 to -15 °C to a solution of 2 g (30 mmol) of sodium azide in 12 mL of acetone/water (1:1). After a few seconds, a yellow liquid phase separated which turned to orange. Then the orange liquid (1,1-dicyano-2,2-diazidoethylene, 7) was dried over molecular sieves and diluted with 10 mL of dried benzene, 1,2-dichloroethane, or toluene. This solution was added to 300 mL of hot (60–65 °C) dry benzene, 1,2-dichloroethane, or toluene under argon; N_2 gas evolution was observed. The reaction was complete after 1 h at the same temperature. The concentration of the solution is about 0.01 M in C_4N_4 based on the yields of subsequent reactions. The IR spectrum of this solution shows the characteristic C=N (1714 cm^{-1}) and CN (2246 and 2240 cm^{-1}) bands. No azide absorption at 2160 cm^{-1} was present. ^{13}C NMR (benzene-d): δ 107.5, 109.3, and 110.15 (3 CN) ppm.

Methyl 3-Aza-2,3-dicyanoacrylate (2). A saturated solution of methyl 3,3-dichloro-2-cyanoacrylate, 8 (500 mg, 2.7 mmol), in acetone was added to a saturated solution of sodium azide (2 g, 0.03 mol) in 10 mL of acetone/water (1:1) at -15 °C. Pale yellow crystals of methyl 3,3-diazido-2-cyanoacrylate (4) (450 mg, 84% yield) were obtained following literature procedures.[14,15] IR (KBr): ν_{max} 2146 (C-N$_3$) cm^{-1}.

A solution of compound 4 in 50 mL of dry benzene or toluene was heated to 55–60 °C under argon atmosphere with stirring for 1 h. The IR spectrum of this solution shows the characteristic C=N stretching (1749 cm^{-1}). ^{1}H NMR benzene-d_6: δ 2.9 and 3.1 (CH$_3$). ^{13}C NMR (benzene-d_6): δ 53.55, 54.01, (CH$_3$), 109.0, 109.4, 110.5, 112.0 (CN), 149.9, 150.55 (C=O) and 152.5 (C=N). The NMR spectra show the presence of both isomers in a 43:57 ratio. MS (DCI): m/e 137 (M + 1)$^+$.

Attempted Synthesis of Diethyl (Cyanoimino)malonate (3). Titanium tetrachloride (0.1 mL) was added to a solution of 0.9 g (0.005 mol) of bis(trimethylsilyl)carbodiimide and diethyl ketomalonate (0.8 g, 0.005 mol) in 50 mL of toluene. A yellow clear solution was obtained. After 3 h of stirring, the IR (solution) showed: ν_{max} 2207 (C≡N), 1755 (C=O), and 1690 (C=N) cm^{-1}. Removal of toluene gave a precipitate; the IR spectrum showed this to be the polymer (no C=N band at 1690 cm^{-1}).

Cycloadducts of 1 and 2 with 2,3-Dimethyl-1,3-butadiene (9 and 10). An excess of 2,3-dimethyl-1,3-butadiene 1,3-butadiene (4 equiv) was added dropwise to benzene solution of 1 or 2 at room temperature with stirring. The greenish yellow solution changed to colorless after 15 min. Stirring was continued for one more hour. After evaporation of the solvent and excess 2,3-dimethyl-1,3-butadiene, the cycloadducts 9 or 10 were obtained. The crude products were recrystallized in ether to give white needles (~60% yield based on 6 or 8).

Cycloadduct 9. Mp: 80–80.5 °C. IR (KBr): ν_{max} 2227 (CN) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.7 and 1.8 (s, 6 H), 2.95 (s, 2 H, CH$_2$), 3.95 (s, 2 H, NCH$_2$). ^{13}C NMR (CDCl$_3$): δ 15.76, 18.38 (Me), 39.58, 50.66, 49.81 (ring C), 110.77, 111.47 (3 CN), 120.12, 122.56 (vinylic C). MS: m/e 186 (M$^+$). Anal. Calcd for C$_{10}$H$_{10}$N$_4$: C, 64.5; H, 5.41; N, 30.09. Found: C, 64.52; H, 5.36; N, 30.13.

Cycloadduct 10. Mp: 81–82 °C; IR (KBr): ν_{max} 2226 (CN), 1756 (C=O) cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 3.96 (CH$_3$O), 3.86 (CH$_2$-NCN), 2.85, 2.75, (2 d, J = 17.7 Hz, CH$_2$) and 1.72 (s, CH$_3$). Anal.

(20) Birkofer, L.; Ritter, A.; Richter, P. *Tetrahedron Lett.* **1968**, 195.

Calcd for C$_{11}$H$_{13}$N$_3$O$_2$: C, 60.26; H, 5.98; N, 19.15. Found: C, 59.92; H, 5.91; N, 19.07.

Cycloaddition of 1 and 2 with Cyclopentadiene (11 and 12). A 4-fold excess of cyclopentadiene was added to the benzene solution of 1 or 2 at room temperature with stirring. A colorless solution was obtained after 1 h. Removal of solvent and recrystallization from ether yielded a white crystalline solid (~50% based on compounds 6 and 8).

Compound 11. IR (KBr): ν_{max} 2221, (C≡N) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 2.1 (2 H, CH$_2$), 4.2, 4.9 (2 H, bridge H's), 6.7 and 6.9 (2 H, vinylic H). Anal. Calcd for C$_9$H$_6$N$_4$: C, 63.52; H, 3.55; N, 32.93. Found: C, 63.75; H, 3.43; N, 33.07.

Compound 12. IR (KBr): ν_{max} 2216, 2161 (C≡N), 1761 (C=O) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.9 (2 H, CH$_2$), 4.3, 4.9 (2 H, bridge H's), 6.8, 6.9 (2 H, vinylic H), and 4.1 (CH$_3$O). Anal. Calcd for C$_{10}$H$_9$N$_3$O$_2$: C, 58.53; H, 5.36; N, 20.48. Found: 58.31; H, 5.29; N, 20.38.

Synthesis of 13. A 5-fold excess of N,N-dimethylaniline was added to a benzene solution of 1 at room temperature with stirring. A red solution formed, which was stirred overnight. The precipitate was filtered off. Recrystallization from glacial acetic acid gave red crystals of 13 (30% yield based on compound 6). IR (KBr): ν_{max} 2173 (CN), 1612 (C=N) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 3.2 (6 H, 2 CH$_3$), 6.8 and 8.0 (4 H, aromatic). Anal. Calcd for C$_{11}$H$_{10}$N$_4$: C, 66.65; H, 5.09; N, 28.27. Found: C, 66.43; H, 5.07; N, 28.43.

Hydrolysis of 13. Sodium hydroxide (1 M, 25 mL) was added to 13 (200 mg, 10 mmol), and the slurry was stirred for 2 days at room temperature. A clear light yellow solution was obtained, which was acidified with 4 N HCl. Filtration gave light yellow crystals of a salt (100 mg). ^{1}H NMR (CDCl$_3$): δ 7.5 (2 H, ring), 6.5 (2 H ring), 2.8 (6 H, 2 CH$_3$).

The salt (50 mg) was dissolved in 2 mL of absolute ethanol, and 1 mL of concentrated HCl was added. The alcoholic solution was refluxed for 2 h. After neutralization with sodium hydroxide, ethyl 4-(dimethylamino)benzoate (14) was obtained. Mp: 63.5–64.5 °C. ^{1}H NMR (CDCl$_3$): δ 7.2, 6.2, 3.6, 2.4 (6 H), 1.7 (3 H). IR (KBr): ν_{max} 1693 (C=O) cm^{-1}, no C=N or CN.

Copolymerization. A 4-fold excess (based on 6 or 8) of p-methoxystyrene was added to benzene solution of 1 or 2 at room temperature under argon atmosphere. The yellow color of the solution changed to dark red, and then after 1 h stirring, a pale yellow color was formed. Removal of benzene gave a viscous material, which was dissolved in an minimal amount of chloroform. The chloroform solution added dropwise to 100 mL of ether with vigorous stirring. The alternating copolymer was obtained as a yellow solid.

Copolymer 15. IR (KBr): ν_{max} 2210, 2100 (CN) cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 6.4–7.4 (broad), 3.6–3.9 (broad). Anal. Calcd for C$_{13}$H$_{10}$N$_4$O: C, 65.53; H, 4.23; N, 23.52. Found: C, 64.22; H, 4.28; N, 22.82.

Copolymer 16. IR (KBr): ν_{max} 2216, 2228 (CN), 1777 (C=O) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 6.9–7.5 (broad, ring), 3.7–4.05 (broad, CH$_3$O), and 3.3–3.6 (broad). Anal. Calcd for C$_{14}$H$_{13}$N$_3$O$_3$: C, 61.98; H, 4.33; N, 15.49. Found: C, 60.94; H, 4.79; N, 15.42.

Registry No. 1, 117533-11-6; 2, 82523-14-6; 4, 82140-87-2; 6, 10472-00-1; 7, 117668-91-4; 8, 13063-44-0; 9, 117668-92-5; 10, 82523-15-7; 11, 117668-93-6; *endo*-12, 124782-10-1; *exo*-12, 124782-11-2; 13, 117668-94-7; 13·HCl, 124782-12-3; 14, 10287-53-3; 15 (copolymer), 117533-12-7; 16 (copolymer), 124782-13-4; cyclopentadiene, 542-92-7; N,N-dimethylaniline, 121-69-7; 2,3-dimethyl-1,3-butadiene, 513-81-5.