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Double Cycloaddition Reaction of Imidazolium Methylides. Intermolecular 1,3-Dipolar and Intramolecular Diels-Alder Cycloaddition Reactions

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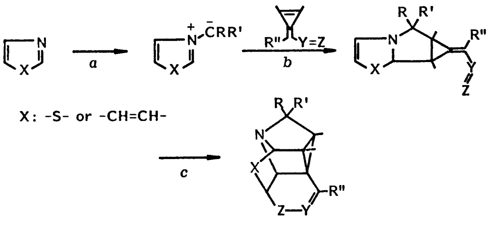
Such imidazolium methylides as imidazolium dicyanomethylide and bis(ethoxycarbonyl)methlide react with the methylenecyclopropenes with unsaturated substituents at the 4-position in the fashion of double cycloaddition reaction, leading to the novel cage compounds, which involves an intermorecular 1,3-dipolar cycloaddition reaction and an intramolecular Diels-Alder reaction.

Since the reaction of thiazolium methylides with the methylenecyclopropenes having unsaturated substituents at the 4-position presented the first example of double cycloaddition reaction that included at least a 1,3-dipolar cycloaddition reaction,[1,2] it has been reported that pyridinium methylides can be also employed in the similar reaction with methylenecyclopropenes leading to the cage compounds.[3]



Scheme 1.

As shown in Scheme 1, these reactions have provided a new methodology for the double functionalization of nitrogen-containing aromatic heterocycles such as thiazole and pyridine: The heterocycles are converted into the corresponding azomethine ylide 1,3-dipoles (the step *a* as the first functionalization), the 1,3-dipolar cycloaddition reaction of the ylides across the endocyclic double bond of methylenecyclopropenes forms the [3+2] cycloadducts leading to the collapse of aromatic character of the starting heterocycles (the step *b* as the second functionalization), and the intramolecular Diels-Alder reaction takes place across the newly formed olefinic double bond giving the cage compounds (the step *c*).

According to the general reaction pattern mentioned above, imidazole would be also doubly functionalized by the ylide formation and the reaction with methylenecyclopropenes having unsaturated substituents at the 4-position, while no examples for the 1,3-dipolar cycloaddition reaction of imidazolium ylides to olefinic dipolarophiles have been reported so far.[4]

This paper describes the first example for the double cycloaddition reaction of imidazolium methylides that react with methylenecyclopropenes having unsaturated substituents at the 4-position leading to the novel cage compounds.

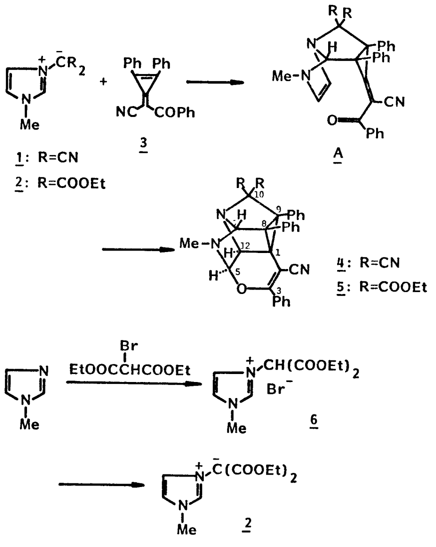
Results and Discussion

The Reaction with 2-Benzoyl-2-(2,3-diphenyl-2-cyclopropenylidene)acetonitrile. The reaction of 1-methyl-1*H*-imidazol-3-ium dicyanomethylide (**1**) with 2-benzoyl-2-(2,3-diphenyl-2-cyclopropenylidene)acetonitrile (**3**) in ethanol under reflux gave the 1:1 adduct **4** as a colorless solid in a good yield (Table 1). The IR spectrum exhibits no carbonyl stretching indicating that the benzoyl group of **3** has participated in a cyclization. The structure of **4** was easily assigned to the pentacyclic cage structure shown in Scheme 2 by comparison of the NMR spectral data with those of the similar cage compounds obtained in the reaction of thiazolium methylides.[1] The ^{1}H-NMR spectrum shows three methine hydrogens, two of which couple each other (J_{5-12}=4.0 Hz), and the ^{13}C-NMR indicates the existence of a cyclopropane ring (28.17, 41.85, and 50.28 ppm as each singlet), three methine carbons (66.18, 88.59, and 97.56 ppm as each doublet), and another quaternary carbon (65.69 ppm as a singlet).

Although the zwitterionic dicyanomethylides of nitrogen-containing heterocycles are stable enough to be isolated and have been conveniently used in the study of cycloaddition reactions, the major problem is their hard solubility in organic solvents. So a new imidazolium methylide, 1-methyl-1*H*-imidazol-3-ium bis(ethoxycarbonyl)methylide (**2**), was synthesized. The reaction of 1-methylimidazole with diethyl 2-bromomalonate in acetone afforded 1-methyl-3-[bis(ethoxycarbonyl)methyl]-1*H*-imidazol-3-ium bromide (**6**) in a quantitative yield. Treatment of the salt **6** with aqueous sodium carbonate gave the expected ylide **2** as a colorless solid also in a quantitative yield. The ylide **2** is less stable than the dicyanomethylide **1**,[5] but readily soluble in aprotic organic solvents such

Table 1. Reaction of imidazolium methylides with methylenecyclopropenes

Reactant		Reaction conditions			Product	Yield
		Temperature	Time/h	Solvent		%
1	**3**	Reflux	29	Ethanol	**4**	76
2	**3**	Reflux	2	THF	**5**	99
7	**8**	Room temperature	4	THF	**9**	28
1	**8**	Reflux	24	Ethanol	**10**	36
					11	30
2	**8**	Reflux	48	THF	**12**	90



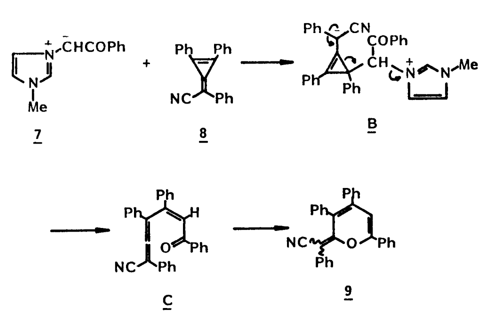
Scheme 2.

as chloroform and tetrahydrofuran.

The imidazolium bis(ethoxycarbonyl)methylide **2** thus synthesized reacted with **3** under reflux in tetrahydrofuran for 2 h to give the similar cage compound **5** in an almost quantitative yield (Table 1). The structure of **5** was confirmed on the basis of the spectral data.

The reaction pathway for the formation of the pentacyclic cage compounds **4** and **5** is illustrated in Scheme 2. It should be emphasized that the imidazolium methylides **1** and **2** have cycloadded stereo- and regioselectively to the endocyclic double bond of the methylenecyclopropene **3** to form the intermediary *endo* [3+2] cycloadducts **A** whose structures are favored for the subsequent intramolecular Diels-Alder cycloaddition reaction.

The Reaction with 2-Phenyl-2-(2,3-diphenyl-2-cyclopropenylidene)acetonitrile. The reaction of 1-methyl-1*H*-imidazol-3-ium phenacylide (**7**), which was generated *in situ* from 1-methyl-3-phenacyl-1*H*-imidazol-3-ium bromide and triethylamine, with 2-phenyl-2-(2,3-diphenyl-2-cyclopropenylidene)acetonitrile (**8**) in tetrahydrofuran at room temperature gave a red-colored product **9** in 28% yield. The product **9** has a molecular formula derived from the 1:1 adduct between **7** and **8** with the loss of 1-methylimidazole, and was determined as 2-(α-cyanobenzylidene)-3,4,6-triphenyl-2*H*-pyran on the basis of the IR (no carbonyl stretching), ^{1}H-NMR (an olefinic singlet at 6.47 ppm), and ^{13}C-NMR spectra (no sp^{3} carbon). The elimination of heterocyclic moiety from the N-ylides of nitrogen-containing heterocycles has been observed quite often.[6] In the reaction of pyridinium phenacylide with 4,4-diacylmethylenecyclopropenes, Eicher has reported the formation of red-colored pyran derivatives as the pyridine-eliminated products.[7] The formation of **9** is explained by the reaction pathway shown in Scheme 3: The nucleophilic addition of the ylide carbon of **7** to the endocyclic double bond of **8** forms the intermediary zwitterion **B**, 1-methylimidazole is kicked out to give the allene intermediate **C**, and finally the 6π-cyclization occurs leading to the isolated product **9**.



Scheme 3.

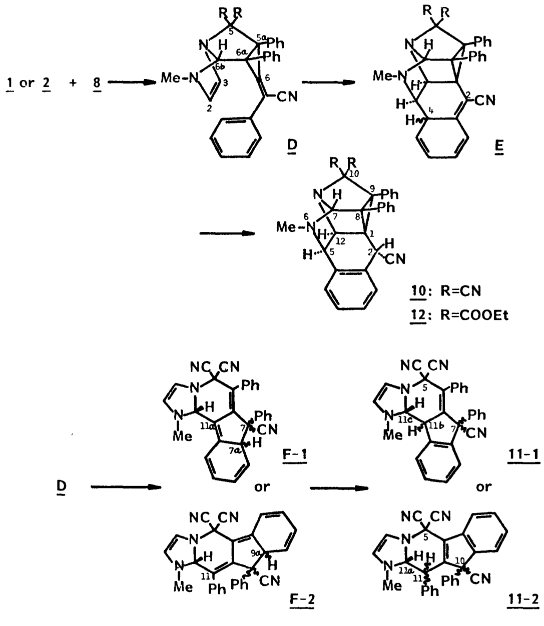
On the other hand, the reaction of the dicyanomethylide **1** with the methylenecyclopropene **8** under reflux in ethanol gave two kinds of the 1:1 adducts **10** and **11** in 36 and 30% yields, respectively. The analysis of the spectral data confirmed the pentacyclic cage structure of **10** and the imidazoindenopyridine structure of **11**.

The ^{1}H-NMR and ^{13}C-NMR spectra of **10** show four methine hydrogens and carbons (4.11^{s}, 4.15^{d} (J=4.0 Hz), 4.50^{d}, and 4.92^{s} ppm in the ^{1}H-NMR, and 27.53, 66.99, 68.10, and 93.17 ppm as each doublet in the ^{13}C-NMR spectra) and three singlet carbons assigned to the carbons of cyclopropane moiety (33.17, 36.93, and 48.14 ppm). The stereochemistry at the 2-position was determined as shown in Scheme 4 on the ground of the high chemical shift of the 2-methine hydrogen.[8]

The ^{1}H-NMR spectrum of **11** shows only two methine hydrogens which couple each other with a coupling constant of 7.0 Hz (5.58 and 6.10 ppm). The ^{13}C-NMR spectrum exhibits two quaternary carbons (67.36 and 68.05 ppm) as well as two methine carbons (40.28 and 94.81 ppm). The absence of a cyclopropane moiety in **11** indicates that the cyclopropane ring and one of the phenyl groups of **8** have interacted to give the product **11**. Although there are two skeletons possible for **11** (the 5,7,11b,11c-tetrahydro-1*H*-imidazo[1,2-*a*]indeno[1,2-*c*]pyridine(**11-1**) and 5,10,11,11a-tetrahydro-1*H*-imidazo[1,2-*a*]indeno[2,1-*d*]pyridine (**11-2**)) on the basis of the reaction modes mentioned later, it was impossible to assign the correct structure.

On the other hand, the bis(ethoxycarbonyl)methylide **2** gave the pentacyclic cage compound **12** as the single product in an excellent yield (Table 1). The spectral data are consistent with the proposed structure.

The reaction of the imidazolium methylides **1** and **2** with the methylenecyclopropene **8** proceeds also stereo- and regioselectively forming the *endo* [3+2] cycloadducts **D** which then cyclize through the intramolecular Diels-Alder reaction to give the other intermediates **E**. A 1,3-hydrogen shift of the 4-methine hydrogen to the 2-position affords the cage compounds **10** and **12**. In the case of the intermediate **D** derived from the dicyanomethylide **1**, another type of cyclization takes place. The Cope rearrangement concerned with the phenyl group at the 6a- or 5a-position leads to the intermediate **F-1** or **F-2**, respectively, while it is not clear which phenyl group has participated in the rearrangement. A 1,3-hydrogen shift of the 7a-hydrogen of **F-1** or a 1,5-hydrogen shift of the 9a-



Scheme 4.

hydrogen of **F-2** gives the product **11-1** or **11-2**, respectively. The similar Cope rearrangement has been observed in the [2+2] cycloadduct of an enamine to **8**.[9]

Experimental

General. Melting points were determined on a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra were taken with a JASCO IRA-1 or a JASCO A-102 spectrometer. ^{1}H-NMR spectra were recorded on a Hitachi R-40 at 90 MHz or a JEOL FX-100 spectrometer at 100 MHz and ^{13}C-NMR spectra were obtained on a JEOL FX-100 instrument at 25.05 MHz. Chemical shifts are expressed in parts per million downfield from tetramethylsilane. Mass spectra were measured with a JEOL JMS-01SG-2 spectrometer at 75 eV of ionization energy. Elementary analyses were performed on a Hitachi 026 CHN analyzer. Thin-layer chromatography (TLC) was accomplished on 0.2-mm precoated plates of silica gel 60 F-254 (Merck) or on 0.2-mm precoated plates of aluminum oxide 60 F-254 type E (Merck). Visualization was with ultraviolet light (254 and 365 nm) and iodine. Preparatory column chromatography was performed on silica gel Wako C-300 (Wako). Solvents were evaporated with a Tokyo Rikakikai rotary vacuum evaporator type V at about 50 °C unless otherwise stated.

Tetrahydrofuran was distilled from sodium immediately before use. Triethylamine was distilled and stored on potassium hydroxide. Acetone was dried over anhydrous potassium carbonate.

Materials. 2-Benzoyl-2-(2,3-diphenyl-2-cyclopropenylidene)acetonitrile(**3**) (pale yellow needles from 2-propanol, mp 168—170 °C (lit,[10]) mp 162—163 °C)) and 2-phenyl-2-(2,3-diphenyl-2-cyclopropenylidene)acetonitrile (**8**) (orange needles from benzene-hexane, mp 178—180 °C (lit,[11]) mp 182—183 °C)) were prepared according to the reported methods. 1-Methyl-1*H*-imidazol-3-ium dicyanomethylide (**1**) (beige leaflets from ethanol, mp 142—143 °C (lit,[12]) mp 143—144 °C)) was synthesized by the reaction of 1-methylimidazole with tetracyanoethylene oxide. 1-Methyl-3-phenacyl-1*H*-imidazol-3-ium bromide (colorless needles from acetonitrile, mp 154 °C (lit,[13]) mp 153—155 °C) was obtained in 96% yield in the reaction of 1-methylimidazole with phenacyl bromide. 1-Methylimidazole and diethyl 2-bromomalonate are commercially avaliable.

*Reaction of 1-Methyl-1*H*-imidazol-3-ium Dicyanomethylide (**1**) with 2-Benzoyl-2-(2,3-diphenyl-2-cyclopropenylidene)acetonitrile (**3**).* A mixture of **1** (73 mg, 0.5 mmol) and **3** (169 mg, 0.5 mmol) in ethanol (20 ml) was refluxed for 29 h during which time all the starting materials were consumed (on TLC). After complete evaporation of the solvent *in vacuo*, the residue was chromatographed over silica gel using benzene as an eluent to give **4** (182 mg, 76%): Colorless needles from ether-hexane, mp 185—188 °C (decomp)). IR (KBr) 2180 cm^{-1} (C≡N); ^{1}H-NMR (CDCl$_3$) δ=2.94 (3H, s, 6-Me), 4.13 (1H, d, $J_{12\text{-}5}$=7.0 Hz, 12-H), 5.13 (1H, s, 7-H), 5.58 (1H, d, $J_{5\text{-}12}$=7.0 Hz, 5-H), and 6.70—7.82 ppm (15H, m, ArH); ^{13}C-NMR (CDCl$_3$) δ=28.17 (s, 1-C), 41.18 (q, 6-Me), 41.85, 50.28 (each s, 8- and 9-C), 65.69 (s, 10-C), 66.18 (d, 12-C), 88.59 (d, 7-C), 97.56 (d, 5-C), 110.71, 116.22 (each s, 10-CN), 121.97 (s, 2-CN), and 168.94 ppm (s, 3-C); MS *m/e* 479 (M$^+$, 4%). Found: C, 77.39; H, 4.41; N, 14.59%. Calcd for $C_{31}H_{21}ON_5$: C, 77.66; H, 4.38; N, 14.67%.

*1-Methyl-1*H*-imidazol-3-ium Bis(ethoxycarbonyl)methylide (**2**).* A mixiture of 1-methylimidazole (2.5 g, 0.03 mol) and diethyl 2-bromomalonate (7.2 g, 0.03 mol) in dry acetone (50 ml) was stirred at room temperature for 24 h. The acetone was evaporated *in vacuo* giving a colorless viscous oil of **6** (9.7 g, 100%). The salt **6** (9.7 g, 0.03 mol) was dissolved in water (5 ml) and treated with saturated aqueous sodium carbonate under vigorous stirring precipitating colorless solid of **2** (7.2 g, 100%): Colorless prisms from chloroform-acetone, mp 164—165 °C. IR (KBr) 1690, 1640 (C=O), and 1580 cm^{-1}; ^{1}H-NMR (CDCl$_3$) δ=1.24 (6H, t, CH$_2$C$\underline{\text{H}}_3$), 3.92 (3H, s, *N*-Me), 4.09 (4H, q, C$\underline{\text{H}}_2$CH$_3$), 7.09 (2H, m, 4- and 5-H), and 8.25 ppm (1H, br, s, 2-H).

*Reaction of **2** with **3**.* A mixture of **2** (120 mg, 0.5 mmol) and **3** (167 mg, 0.5 mmol) in dry tetrahydrofuran (20 ml) was refluxed until **3** no longer showed its spot on a TLC plate (2 h). The tetrahydrofuran was evaporated *in vacuo* and then the residue was chromatographed over silica gel using benzene as an eluent to give **5** (284 mg, 99%): Colorless prisms from ether-light petroleum, mp 175 °C. IR (KBr) 2204 (C≡N) and 1738 cm^{-1} (C=O); ^{1}H-NMR (CDCl$_3$) δ=1.02, 1.19 (each 3H, t, 10-COOCH$_2$-C$\underline{\text{H}}_3$), 2.94 (3H, s, 6-Me), 3.97 (1H, d, $J_{12\text{-}5}$=4.0 Hz, 12-H), 4.12, 4.22 (each 2H, q, 10-COOC$\underline{\text{H}}_2$CH$_3$), 5.40 (1H, s, 7-H), 5.54 (1H, d, $J_{5\text{-}12}$=4.0 Hz, 5-H), and 6.60—7.58 ppm (15H, m, ArH); ^{13}C-NMR (CDCl$_3$) δ=13.56, 13.74 (each q, 10-COOCH$_2$$\underline{\text{C}}H_3$), 29.53 (s, 1-C), 41.10 (q, 6-Me), 44.09, 47.61 (each s, 8- and 9-C), 61.82 (t, 10-COOCH$_2$CH$_3$), 65.52 (d, 12-C), 85.30 (s, 10-C), 87.77 (d, 7-C), 97.93 (d, 5-C), 117.18 (s, 2-CN), 166.15 (s, 10-$\underline{\text{C}}$OOEt), and 168.26 ppm (s, 3-C); MS *m/e* 573 (M$^+$, 63%) and 500 (M$^+$−COOEt, 33%). Found: C, 73.00; H, 5.45; N, 7.33%. Calcd for $C_{35}H_{31}O_5N_3$: C, 73.28; H, 5.45; N, 7.33%.

*Reaction of 1-Methyl-1*H*-imidazol-3-ium Phenacylide (**7**) with 2-Phenyl-2-(2,3-diphenyl-2-cyclopropenylidene)acetonitrile (**8**).* To a stirred suspension of 1-methyl-3-phenacyl-1*H*-imidazol-3-ium bromide (141 mg, 0.5 mmol) and **8** (153 mg, 0.5 mmol) in 25 ml of dry tetrahydrofuran was added dropwise triethylamine (0.07 ml, 0.5 mmol). After the mixture was stirred at room temperature for 4 h, a colorless solid precipitated (triethylammonium bromide) was filtered off and washed with 5 ml of tetrahydrofuran. The combined filtrate and washing were evaporated *in vacuo*. The residue was chromatographed over silica gel using benzene as an eluent to afford **3** (60 mg, 28%): Red needles from 2-propanol, mp 187 °C. IR (KBr) 2250 cm^{-1} (C≡N); ^{1}H-NMR ($CDCl_3$) δ=6.47 (1H, s, 5-H) and 6.80—7.85 ppm (20H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ=104.95 (s, CN), 124.90 (d, 5-C), 127.36 (s, =$\underline{C}$(CN)Ph), 143.33 (s, 4-C), 154.68 (s, 6-C), and 161.40 ppm (s, 2-C); MS *m/e* 423 (M^+, base peak), 105 ($PhCO^+$, 57%), and 77 (Ph^+, 37%). Found: C, 88.12; H, 5.09; N, 3.56%. Calcd for $C_{31}H_{21}ON$: C, 87.94; H, 4.96; N, 3.31%.

*Reaction of **1** with **8**.* A solution of **1** (73 mg, 0.5 mmol) and **8** (153 mg, 0.5 mmol) in ethanol (20 ml) was refluxed for 24 h. No trace of **8** was detected on a TLC plate after 24 h. The solvent was completely removed off by evaporation *in vacuo*. The residue was chromatographed over silica gel using benzene as an eluent. The first colorless fraction gave **10** (82 mg, 36%) and the second yellow fraction afforded **11** (68 mg, 30%).

10: Colorless needles from ether-light petroleum, mp 251—252 °C (decomp). IR (KBr) 2250 cm^{-1} (C≡N); ^{1}H-NMR ($CDCl_3$) δ=2.81 (3H, s, 6-Me), 4.11 (1H, s, 2-H), 4.15 (1H, d, J_{12-5}=4.0 Hz, 12-H), 4.50 (1H, d, J_{5-12}=4.0 Hz, 5-H), 4.92 (1H, s, 7-H), and 6.40—7.64 ppm (14H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ=27.53 (d, 2-C), 33.17 (s, 1-C), 36.93, 48.14 (each s, 8- and 9-C), 44.56 (q, 6-Me), 63.30 (s, 10-C), 66.99 (d, 12-C), 68.10 (d, 5-C), 93.17 (d, 7-C), 111.08, 111.95 (each s, 10-CN), and 119.00 ppm (s, 2-CN); MS *m/e* 451 (M^+, base peak). Found: C, 79.91; H, 4.70; N, 15.55%. Calcd for $C_{30}H_{21}N_5$: C, 79.80; H, 4.69; N, 15.51%.

11: Yellow prisms from ether-light petroleum, mp 132—133 °C. IR (KBr) 2250 cm^{-1} (C≡N); ^{1}H-NMR ($CDCl_3$) δ=2.84 (3H, s, 1-Me), 5.58 (1H, d, J=7.0 Hz, CH), 6.10 (1H, d, J=7.0 Hz, CH), and 6.75—7.64 ppm (16H, m, ArH, 2- and 3-H); ^{13}C-NMR ($CDCl_3$) δ=40.28 (d, CH), 44.44 (q, 1-Me), 67.36, 68.05 (each s, quart-C), 94.81 (d, CH), 111.72, 114.42, and 118.34 ppm (each s, CN); MS *m/e* 451 (M^+, base peak). Found: C, 79.63; H, 4.60; N, 15.53%. Calcd for $C_{30}H_{21}N_5$: C, 79.80; H, 4.69; N, 15.51%.

*Reaction of **2** with **8**.* A mixture of **2** (120 mg, 0.5 mmol) and **8** (153 mg, 0.5 mmol) in dry tetrahydrofuran (20 ml) was refluxed for 48 h. The tetrahydrofuran was eveporated *in vacuo* and the residue was chromatographed over silica gel using benzene as an eluent to give **12** (245 mg, 90%): Colorless prisms from ether-light petroleum, mp 192 °C. IR (KBr) 2220 (C≡N) and 1740 cm^{-1} (C=O); ^{1}H-NMR δ=1.13, 1.19 (each 3H, t, 10-$COOCH_2C\underline{H}_3$), 2.77 (3H, s, 6-Me), 4.02 (1H, d, J_{12-5}=4.3 Hz, 12-H), 4.14, 4.23 (each 2H, q, 10-$COOC\underline{H}_2CH_3$), 4.16 (1H, s, 2-H), 4.40 (1H, d, J_{5-12}=4.3 Hz, 5-H), 5.11 (1H, s, 7-H), and 6.50—7.50 ppm (14H, m, ArH); ^{13}C-NMR ($CDCl_3$) δ=13.77 (q, 10-$COOCH_2\underline{C}H_3$), 28.86 (d, 2-C), 33.98 (s, 1-C), 39.16, 45.31 (each s, 8- and 9-C), 44.82 (q, 6-Me), 62.01, 62.16 (each t, 10-$COO\underline{C}H_2CH_3$), 66.36 (d, 12-C), 67.53 (d, 5-C), 83.25 (s, 10-C), 92.62 (d, 7-C), 120.16 (s, 2-CN), 167.09 and 167.72 ppm (each s, 10-$\underline{C}OOEt$); *m/e* 545 (M^+, 15%) and 472 ($M^+-COOEt$, base peak). Found: C, 74.82; H, 6.12; 7.51%. Calcd for $C_{34}H_{31}O_4N_3$: C, 74.84; H, 5.73; N, 7.70%.

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4) The cycloaddition reaction of imidazolium methylides to acetylenic dipolarophiles has been reported (see Ref. 13). The only example for the reaction of benzimidazolium ylide with acrylonitrile (I. Zugravescu, J. Herden, and I. Druta, *Rev. Roumaine de Chim.*, **19**, 659 (1974)) and some reports of the reaction with acetylenic dipolarophiles (H. Ogura and K. Kikuchi, *J. Org. Chem.*, **37**, 2679 (1972); I. Zugravescu, J. Herdan, and I. Druta, *Rev. Roumaine de Chim.*, **19**, 649 (1974); O. Meth-Cohn, *Tetrahedron Lett.*, **1975**, 413) are known.

5) The purification of the bis(ethoxycarbonyl)methylide **2** by recrystallization failed. Once the ylide **2** is dissolved in organic solvents, it hardly crystallizes again. Evaporation of the solvents gives a pasty material whose ^{1}H-NMR spectrum, however, is identical to that of **2**.

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8) The reaction of thiazolium dicyanomethylide with **8** afforded two stereoisomeric cage compounds in which the 2-methine hydrogens were observed at 4.29 and 5.03 ppm (see Ref. 2).

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