Synthesis of 5- and 7-(Dicyanomethylene)-2,3-dihydrocyclohepta-1,4-dithiins, "Push-Pull" Heptafulvene Derivatives. 8,8-Dicyanoheptafulvenes from α-Bromomalononitrile and Cycloheptatrienylium Salt

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(Received June 14, 1993)

Treatment of 2,3-dihydro-4a*H*-cyclohepta-1,4-dithiin with triphenylmethyl tetrafluoroborate followed by condensation with α-bromomalononitrile in pyridine afforded 5- and 7-(dicyanomethylene)-2,3-dihydrocyclohepta-1,4-dithiins in good yields. When changing the solvent to acetonitrile, the products obtained were 5- and 6-(2,2-dicyanoethyl)-2,3-dihydro-1,4-benzodithiins. This new method was applicable to the general synthesis of dicyanoheptafulvenes from tropylium salts.

Previously, we synthesized 3,4-diacetoxy-8,8-dimethylheptafulvene (**1**),[1] which is stable enough to isolate and represents non-electron-withdrawing 8,8-disubstituted derivatives. Unlike other heptafulvenes with electron-withdrawing substituents on C-8, e. g., the parent 8,8-dicyanoheptafulvene (**2**),[2,3] the X-ray crystallographic analysis of the structure[1] revealed a rather normal bond length for the exocyclic C=C bond. Since the bond lengths of the exocyclic C=C bond have been regarded as a measure for the polarized aromatic character of the derivatives,[4] the observed bond length of **1** is consistent with that view, and the chemical shifts of the methyl groups at C-8, appearing at a considerably higher field ($\delta=1.73$ in deuteriochloroform) should suggest a diminished contribution of the polarized structure (Chart 1).

In this respect, it is interesting to compare the physicochemical properties of the "push-pull"[5] heptafulvenes having both electron-withdrawing and electron-releasing substituents, 5-(dicyanomethylene)-2,3-dihydro-5*H*-cyclohepta-1,4-dithiin (**3**) and 7-(dicyanomethylene)-2,3-dihydro-7*H*-cyclohepta-1,4-dithiin (**4**), with other heptafulvenes. Herein, we discuss the synthetic aspects of these "push-pull" heptafulvenes (**3** and **4**).[6]

Results and Discussion

Synthesis of 5- and 7-(Dicyanomethylene)-2,3-dihydrocyclohepta-1,4-dithiins. Tropone (**5**) was treated with 1,2-ethanedithiol and boron trifluoride to give 2,3-dihydro-4a*H*-cyclohepta-1,4-dithiin (**6**),[7] which was treated with triphenylmethyl tetrafluoroborate (**7**)[8] to instantly precipitate (1,2-ethylenedithio)cycloheptatrienylium tetrafluoroborate (**8**). Subsequent treatment of **8** with α-bromomalononitrile (**9**) in acetonitrile afforded two ring-contracted styrene derivatives, 5- and 6-(2,2-dicyanoethenyl)-1,4-benzodithiins (**10** and **11**). However, the reaction in pyridine gave the desired **3** and **4** in a good combined yield (Scheme 1).[9]

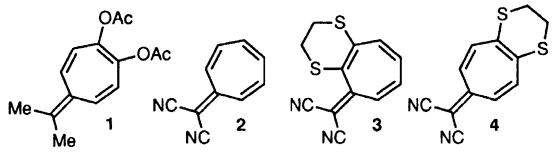


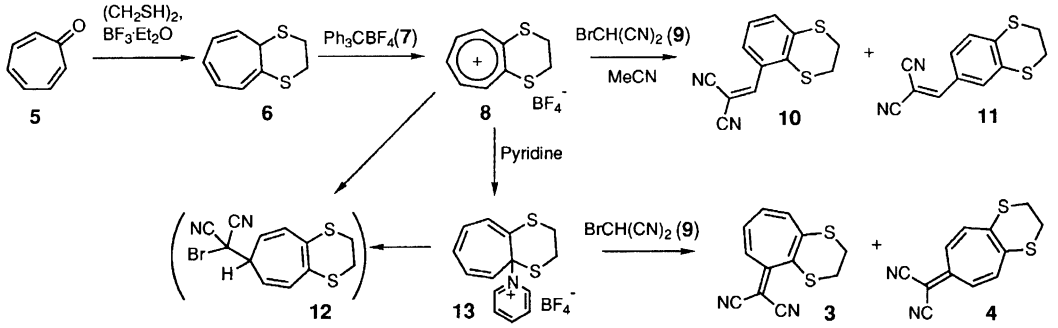
Chart 1.

When the reaction was quenched before completion, an intermediate α-bromomalonyl derivative (**12**) was obtained from both solvents. An important observation was the co-occurrence of **10** and **11**. This strongly suggests that the ring-contraction of **12** to form **10** and **11** occurred during the work-up.

This contrasting result prompted us to investigate the ^{1}H NMR spectral behaviors of **8** in both solvents. In acetonitrile-d_3, **8** revealed signals typical of a 1,2-disubstituted cycloheptatrienylium derivative. But, an addition of pyridine-d_5 into the solution caused a dramatic change in the NMR signals; the ethylenedithio proton singlet at $\delta=3.65$ (4H) changed to multiplets at ca. 3.1 to 3.3, indicating the loss of a symmetrical structure element. The low-field signals showed a five consecutive proton system, i. e., 6.52, 6.42, 6.18, 5.90, and 4.57, whose chemical shifts indicated the non-aromatic character of the seven-membered ring to suggest the formation of a cycloheptatriene system. This is consistent with the formation of 1-(8,11-dithiabicyclo[5.4.0]undeca-2,4,6-trien-1-yl)pyridinium tetrafluoroborate (**13**) (Fig. 1).

The time course of this change was also monitored UV-spectroscopically. As shown in Fig. 2, the UV spectrum of **8**, λ_{max}^{MeCN} at 306 and 447 nm was gradually changed by addition of one drop of pyridine to λ_{max}^{MeCN} at 333 nm, which is appropriate for **12**.

Obviously, this new method of synthesis should be extended to the heptafulvenes in general; i. e., similar treatment of cycloheptatrienylium tetrafluoroborate (**14**) with **9** in pyridine afforded **2** in 96% yield. Again, this combination of the reaction in acetonitrile gave β,β-dicyanostyrene (**15**)[10] in 87% yield (Scheme 2).



Scheme 1.

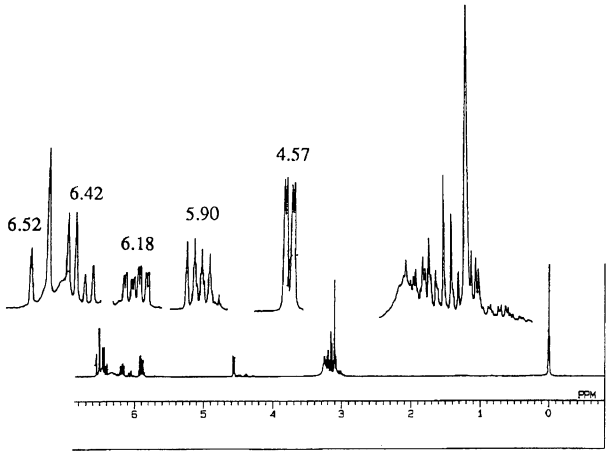


Fig. 1. The ^{1}H NMR spectrum of **13** in pyridine-d_5 (270 MHz).

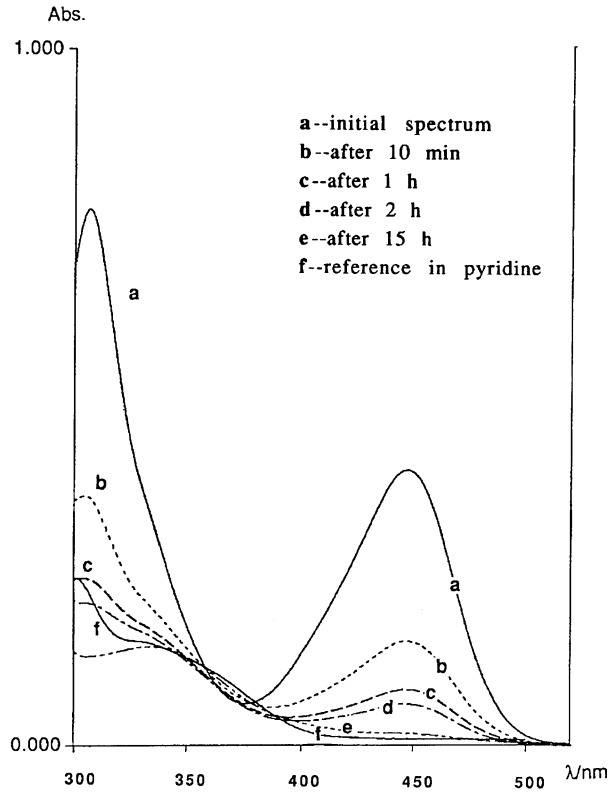


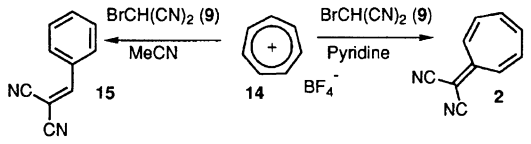
Fig. 2. Time course of UV spectral change of **8** in acetonitrile by adding one drop of pyridine.

The formation of styrene derivatives **10** and **11** from **8** and **9** can be explained in terms of norcaradiene intermediates.[11,12] On the other hand, the formation of heptafulvenes **3** and **4** in pyridine proceeded via the same intermediates as in the case of the reaction in acetonitrile, i. e., a cycloheptatriene (**12**) and its isomer, but the product distributions were entirely different. In the acidic media, the bromine atom on the quaternary dicyanomethyl carbon should be dissociated very easily from the norcaradiene valence isomer as a bromide ion, while under basic conditions, such a dissociation process should not be favored, and the thermal [1,5] sigmatropic hydrogen shift should become operative. Subsequent elimination of hydrogen bromide with the base (pyridine) should be straightforward (Scheme 3). Recently, we have demonstrated heptafulvene formation from sterically-hindered tropones and active methylene derivatives via a remote substitution sequence.[13]

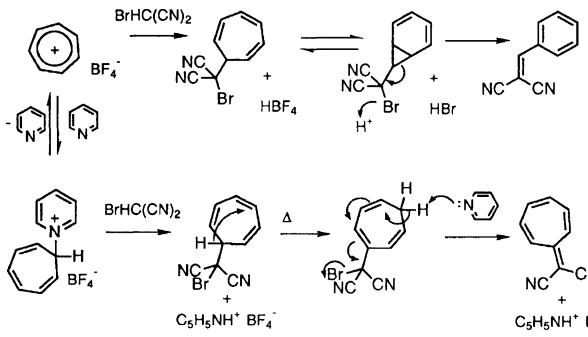
In order to compare the physical properties of **3** and **4**, an oxygen analogue of **4**, 7-(dicyanomethylene)-2,3-dihydro-7*H*-cyclohepta-1,4-dioxin (**16**), was prepared from 2-(2-hydroxyethoxy)-5-hydroxytropone (**17**).[14] Thus, upon treatment with diethyl azodicarboxylate (**18**) and triphenylphosphine, **17** afforded 2,3-dihydro-7*H*-cyclohepta-1,4-dioxin-7-one (**19**) in 97% yield. Treatment of **19** with malononitrile (**20**) in refluxing acetic anhydride quantitatively formed the desired **16** (Scheme 4).

The ^{13}C NMR Spectral Comparison of 3, 4, 2, and 16. In general, the polarized 6π-aromatic contribution of heptafulvenes can be evaluated by means of the chemical shift difference ($\Delta\delta$) of the carbons on the exocyclic C=C bond and the bond length of the exocyclic C=C bond, which could be obtained from the X-ray diffraction study. However, the data obtained from X-ray crystallography, containing the interaction terms in the crystalline state, may not represent the structural properties of the isolated molecule. Therefore, the $\Delta\delta$ values obtained from those dissolved in inert solvents are more reliable to evaluate the aromatic character of the isolated molecule.

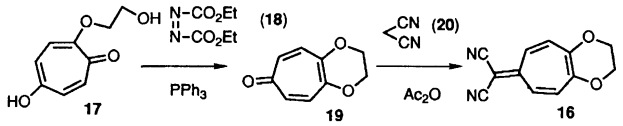
Table 1 compiles the NMR data of several 8,8-disub-



Scheme 2.



Scheme 3.



Scheme 4.

Table 1. ^{13}C NMR Chemical Shift Differences of the Carbons on the Exocyclic C=C

	2	16	4	3	1
δ(C-7)	163.7	159.8	160.6	164.7	136.6
δ(C-8)	70.1	65.1	68.7	80.1	127.7
$\Delta\delta$	93.6	94.7	91.9	84.6	8.9

stituted derivatives. Except for **1**, those derivatives having electron-withdrawing substituents show a considerable degree of polarization as the $\Delta\delta$ is more than 80 ppm. In this regard, dioxa analogue **16** has the highest electron density at the C-8 as having the highest signal ascribable to C-8 (δ=65.1), and that of dithia analogue **4** is still higher than that of unsubstituted **2**. This is attributable to the electromeric effect of ethereal oxygen and sulfur atoms. On the other hand, another dithia compound **3**, shown to be nonplanar by X-ray crystallographic analysis,[6] revealed a C-7 (δ=164.7) chemical shift similar to that of unsubstituted **2** (δ=163.7), but the chemical shift of its C-8 (δ=80.1) appeared at a considerably lower field than those of **2**, **4**, and **16** to make the smallest $\Delta\delta$. Consequently, **2**, **4**, and **16** have almost the same degree of polarized electronic structures, but **3** is concluded to have a diminished polarization as a result of its nonplanar structure.

This was also parallel with the summations of the chemical shift figures of the seven-membered rings ($\Sigma\delta$); i. e., 987.1 for **2**, 978.6 for **16**, and 975.8 for **4**, all similar to each other, but only 963.1 for **3**.

Therefore, introduction of heteroatoms into 8,8-dicyanoheptafulvenes caused little change in their electronic structures; they still retain the fundamental electronic properties of stabilized heptafulvenes. And, these polarized molecules should be promising organic functional molecules. One such example is a mercurophilic property of dithio-crown ether derivatives of heptafulvenes to enable a reversible complexation as shown independently.[15] The X-ray crystallographic analysis of **3** and **4** revealed that the bond lengths of the exocyclic C=C bond of **3** and **4** are somewhat shorter than that of **2**.[6]

Conclusion. The present method has brought a great improvement in synthesizing heptafulvenes. There are several methods with general applicability; a) thermolysis of 1:2-condensates of tropylium salts and active methylene compounds,[3] b) heating a mixture of tropones and active methylene compounds in acetic anhydride,[2] c) condensation of hydroxytropylium salt and active methylene compounds,[16] d) fragmentation of the [8+2] cycloadducts of tropothione to tetracyanoethene,[17] or e) decarboxylative fragmentation of the [2+2] cycloadducts derived from tropones and ketenes.[18] Moreover, conjugated homologues can be prepared by the phosphoryl trichloride-condensation of methylcycloheptatrienylium ion to 3-aminoacrylaldehyde followed by treatment with **20**.[19] However, these methods all suffer restrictions from a preparative point of view. The theoretical yield of heptafulvenes is 50% from the starting seven-membered materials, cycloheptatrienes, since tropones are most conveniently prepared by acid-catalyzed disproportionation of the bis(2,4,6-cycloheptatrienyl)ethers, and hydroxy(or acyloxy)tropylium salts are equivalent to tropones.[20] In addition, preparation of some of those starting materials requires a lengthy multistep sequence. The present method is therefore of great value from the preparative point of view.

Utilization of these "push-pull" heptafulvenes as functional compounds will be independently reported in the future.

Experimental

The elemental analyses were carried out by Mrs. Y. Hatazoe of the Institute of Advanced Material Study, Kyushu University. The melting points were measured with a Yanagimoto Micro Melting Point Apparatus and are uncorrected. The NMR spectra were measured by means of JEOL FX 100 Model and GSX 270H Model spectrometers in $CDCl_3$, unless otherwise stated; the chemical shifts are expressed in δ units. The mass spectra were measured with a JEOL 01SG-2 spectrometer. The IR spectra were taken as KBr disks for crystalline compounds or as liquid films inserted between NaCl plates for oily compounds, using a JASCO IR-A102 spectrometer. The UV spectra were measured using Hitachi U-3200 and U-3410 spectrophotometers. The stationary phase for column chromatography was Wakogel C-300 and the eluent was a mixture of $CHCl_3$, hexane, and EtOAc.

Reaction of 6 with 7. Formation of 8. To a CH_2Cl_2 solution (25 cm^3) of **6** and **7** (8.80 g, 48.4 mmol), prepared from **5** and 1,2-ethanedithiol and $BF_3 \cdot Et_2O$,[7] was added **7** (16.7 g; 50.6 mmol)[8] at room temperature. Instantly precipitated **8** [orange crystals, mp 158 °C (decomp), 8.75 g, 67.5%. Found: C, 40.31; H, 3.51%. Calcd for $C_9H_9S_2BF_4$: C, 40.32; H, 3.38%. ^{1}H NMR (CD_3CN) δ=3.65 (4H, s), 8.08 (2H, dd, J=10.6, 9.2 Hz), 8.21 (1H, t, J=9.2 Hz), and 8.45 (2H, d, J=10.6 Hz). ^{13}C NMR (CD_3CN) δ=31.4 (2C), 143.9 (2C), 147.0 (2C), 148.8 (2C), and 169.0. IR ν 2982, 2950, 2920, 1482, 1420, 1299, 1262, 1254, 1243, 1051, 942, 754, 581, and 520 cm^{-1}. UV λ_{max}^{MeOH} (0.5 M HCl)(1 M= 1 mol dm^{-3})=222 nm (ε=11600), 252 (8600), 309 (18800), and 449 (9800). λ_{max}^{MeCN}=221 nm (ε=12400), 250 (8500), 306 (19700), and 447 (10100)] was practically pure and was used without further purification.

Reaction of 8 with 9 in MeCN. Formation of 10 and 11. a) To an MeCN solution (1 cm^3) of **8** (52.8 mg) was added **9** (29 mg) and the mixture was heated at 80 °C for 3 h. The mixture was then heated in vacuo, and the residue thus obtained was purified via silica-gel column and high-pressure liquid chromatography to give **10**[yellow crystals, mp 133—133.5 °C, 2.5 mg, 5%. ^{1}H NMR δ=3.31 (4H, s), 7.20 (1H, dd, J=8.1, 7.7 Hz), 7.43 (1H, d, J=7.7 Hz), 7.77 (1H, d, J=8.1 Hz), and 8.29 (1H, s). ^{13}C NMR δ=29.9, 30.7, 85.4, 112.1, 113.5, 125.6, 126.3, 130.6, 133.4, 135.6, 135.9, and 156.4. MS m/z, 245 ($(M+1)^+$, 16), 244 (M^+, 100), 229 (81), 216 (35), 184 (30), 172 (23), 146 (16), and 145 (16). IR ν 2924, 2224, 1580, 1564, 1392, 1252, 764, 713, and 616 cm^{-1}. λ_{max}^{MeOH}=214 nm (ε=10200), 245 (14100), 273 (13800), 342 (9000), and 413 (1700)] and **11** [yellow crystals, mp 158—160 °C, 32.0 mg, 66%. Found: C, 59.32; H, 3.39; N, 11.53%. Calcd for $C_{12}H_8N_2S_2$: C, 58.99; H, 3.30, N, 11.46%. ^{1}H NMR δ=3.26—3.43 (4H, m), 7.24 (1H, d, J=8.4 Hz), 7.53 (1H, d, J=2.0 Hz), 7.56 (1H, s), and 7.60 (1H, dd, J=8.4, 2.0 Hz). ^{13}C NMR δ=27.5, 29.5, 81.2, 112.8, 114.0, 126.1, 127.6, 129.0, 131.3, 132.0, 149.6, and 158.2. MS m/z, 246 ($(M+2)^+$, 10), 245 ($(M+1)^+$, 15), 244 (M^+, 100), 231 (9), 229 (91), 216 (22), 189 (12), and 69 (12). IR ν 2926, 2220, 1567, 1524, 1468, 1416, 1394, 1289, 1217, 1116, 1043, 871, 817, and 621 cm^{-1}. UV λ_{max}^{MeOH}=215 nm (ε=8500), 242 (8900), 259 (11000), 289 (15900), 356 (17900), and 398 (15200)].

b) To an MeCN solution (2 cm^3) of **8** (20 mg) was added **9** (11 mg) and the mixture was stirred at room temperature for 3 h. The solvent was then evaporated in vacuo, and the residue thus obtained was purified via silica-gel column and high-pressure liquid chromatography to give **10** (7 mg, 38%), **11** (2 mg, 11%), and **12** [a colorless oil, 4 mg, 17%. ^{1}H NMR δ=2.59 (1H, tt, J=5.9, 1.5 Hz), 3.08—3.18 (2H, m), 3.29—3.39 (2H, m), 5.39 (2H, dd, J=9.4, 5.9 Hz), and 6.14 (2H, dd, J=9.4, 1.5 Hz)].

Reaction of 8 with 9 in Pyridine. Formation of 3 and 4. To a pyridine solution (20 cm^3) of **8** (1.90 g) was added **9** (1.05 g) dropwise and the mixture was heated at 80 °C for 3 h. The mixture was then acidified with dil HCl and extracted with EtOAc. The organic extract was then dried over Na_2SO_4 and evaporated in vacuo. The residue, thus obtained, was chromatographed on a silica-gel column to give **3** [red needles, mp 168—169 °C, 673.0 mg, 39%. Found: C, 59.04; H, 3.31; N, 11.21%. Calcd for $C_{12}H_8N_2S_2$: C, 58.99; H, 3.30; N, 11.46%. ^{1}H NMR δ=3.30—3.41 (4H, m), 6.59 (1H, ddd, J=10.9, 7.0, 1.5 Hz), 6.76 (1H, dd, J=10.9, 1.5 Hz), 6.77 (1H, ddd, J=11.4, 7.0, 1.5 Hz), and 6.91 (1H, dd, J=11.4, 1.5 Hz). ^{13}C NMR δ=32.0, 32.3, 80.1, 113.4, 113.6, 127.3, 127.7, 130.4, 133.4, 135.5, 144.1, and 164.7. MS m/z, 246 ($(M+2)^+$, 88), 245 ($(M+1)^+$, 14), 244 (M^+, 88), 217 (16), 216 (100), 189 (14), 140 (16), 69 (12), and 45 (11). IR ν 2924, 2204, 1620, 1484, 1439, 1399, 1322, 1232, 1176, 1058, 970, 927, 901, 821, 771, 683, 671, and 625 cm^{-1}. UV $\lambda_{max}^{CHCl_3}$=302 nm (ε=11200), 330 (10600), and 445 (9800)] and **4** [red crystals, mp 289—290 °C, 1.028 g, 59%. Found: C, 58.89; H, 3.27; N, 11.18%. ^{1}H NMR δ=3.35 (4H, s), 6.65 (2H, dm, J=12.5 Hz), and 6.98 (2H, dm, J=12.5 Hz). ^{13}C NMR δ=29.4 (2C), 69.7, 114.9 (2C), 128.0 (2C), 139.4 (2C), 140.2 (2C), and 160.6. MS m/z, 245 ($(M+1)^+$, 16), 244 (M^+, 100), 216 (50), 189 (13), 184 (13), 69 (18), and 45 (15). IR ν 2974, 2202, 1615, 1566, 1455, 1398, 1309, 1283, 1211, 1102, 1038, 872, 840, 597, and 524 cm^{-1}. UV $\lambda_{max}^{CHCl_3}$=297 nm (ε=16800), 308 (16300), 348 (5800), 363 (4200), 454 (28300), and 495 (13400)].

Isolation of 12 from the Reaction of 8 with 9 in Pyridine. To a stirred pyridine solution (2 cm^3) of **8** (67 mg) was added **9** (37 mg) dropwise at 0 °C in a 30-min period and then kept for 5 min. The mixture was then acidified with dil HCl and extracted with $CHCl_3$. The organic extract was then dried over Na_2SO_4 and evaporated in vacuo. The residue, thus obtained, was chromatographed on a silica-gel column to give **3** (17 mg, 28%), **4** (21 mg, 34%), **10** (2 mg, 3%), **11** (3 mg, 5%), and **12** (7 mg, 9%).

Synthesis of 2 from 14 and 9. To a stirred pyridine solution (5 cm^3) of **14** (178 mg) was added **9** (145 mg) dropwise at 0—5 °C for 30 min. The mixture was gradually warmed to room temperature and stirred for additional 3 h, after which the mixture was acidified with dil HCl at 0—5 °C and extracted with EtOAc. The organic extract was dried over Na_2SO_4 and evaporated in vacuo. The residue thus obtained was chromatographed on a silica-gel column to give **2**[3] [red needles, mp 198—199 °C (lit,[3] 199—200 °C), 147.5 mg, 96%. ^{1}H NMR δ=6.88—7.00 (4H, m) and 7.34 (2H, dm, J=12.1 Hz). ^{13}C NMR δ=70.1, 114.6 (2C), 135.4 (2C), 137.4 (2C), 138.9 (2C), and 163.7].

Reaction of 14 and 9 in MeCN. Formation of 15. To a stirred MeCN solution (3 cm^3) of **14** (178 mg) was added **9** (145 mg) at 25 °C for 18 h. The mixture was evaporated in vacuo to remove the voltatile material. The residue was chromatographed on a silica-gel column to give **15** [pale yellow crystals, mp 82—82.5 °C, 134 mg; 87%. ^{1}H NMR δ=7.54 (2H, tt, J=7.5, 1.8 Hz), 7.64 (1H, tt, J= 7.5, 1.8 Hz), 7.79 (1H, s), and 7.90 (2H, dt, J=7.5, 1.8 Hz). ^{13}C NMR δ=82.8, 112.5, 113.6, 129.6 (2C), 130.7 (2C), 130.9, 134.6, and 159.9. MS m/z, 154 (M^+, 100), 127 (60), 103 (71), 100 (16), 76 (20), 75 (13), 51 (21), and 50 (21). IR ν 3032, 2222, 1100, 957, 755, 678, 616, and 518 cm^{-1}. UV λ_{max}^{MeOH}=202 nm (ε=8600), 224 (8400), 229 (7800), and 305 (21600)], which was identical to the authentic sample[10] in every respect.

Reaction of 17 with 18. Formation of 19. A suspension of **17**[14] (50 mg) and Ph_3P (110 mg) in anhydrous THF (1 cm^3) was treated with an anhydrous THF solution (1 cm^3) of **18** (73 mg). After being stirred for 3 h at room temperature, the mixture was heated in vacuo to remove the volatile material, and the residue was chromatographed on a silica-gel column to give **19** [colorless crystals, mp 151—

152 °C, 43 mg, 95%. Found: C, 65.85; H, 4.91%. Calcd for $C_9H_8O_3$: C, 65.85; H, 4.88%. ^{1}H NMR δ=4.25 (4H, s), 6.78 (2H, dm, J=12.8 Hz), and 6.99 (2H, dm, J=12.8 Hz). ^{13}C NMR δ=63.8 (2C), 133.5 (2C), 134.2 (2C), 144.3 (2C), and 185.4. IR ν 1640, 1560, 1540, 1265, 1210, 1105, and 1050 cm^{-1}. UV λ_{max}^{MeOH}=236 nm (ε=18400) and 353 (16200)].

Ac_2O-Mediated Condensation of 19 and 20. Formation of 16. An Ac_2O solution of **19** (28 mg) and **20** (35 mg) was refluxed for 1.5 h. After heating the mixture in vacuo to remove the volatile material, the residue was chromatographed on a silica-gel column to give **16** [reddish crystals, mp 275—276 °C, 35 mg, 97%. Found: C, 67.92; H, 3.80; N, 13.20%. Calcd for $C_{12}H_8O_2N_2$: C, 68.08; H, 3.66; N, 13.12%. ^{1}H NMR δ=4.30 (4H, s), 6.87 (2H, dm, J=12.8 Hz), and 7.18 (2H, dm, J=12.8 Hz). ^{13}C NMR δ=64.0 (2C), 65.1, 115.8 (2C), 128.1 (2C), 134.3 (2C), 147.0 (2C), and 159.8. IR ν 3100—2800, 2200, 1520, 1490, 1400, and 1250—1190 cm^{-1}. UV λ_{max}^{MeOH}=246 nm (ε=16100), 286 (4500), and 440 (26100)].

We thank Mr. Tadahiko Kubota, M. Eng., for his technical assistance in preparing **16**.

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9) In this respect, it is worth noting that Kitahara et al. observed a rearrangement of **2** to β,β-dicyanostyrene upon a base treatment (Y. Kitahara, K. Doi, and T. Sato, "Oral Presentation at the Hokkaido Regional Meetings of the Chem. Soc. of Japan," Sapporo, (August, 1960)). In addition, it seems that they have also obtained **2** from **13** and **9**, although no detailed information is available. Cf.: T. Nozoe and T. Asao, "Comprehensive Organic Chemistry," ed by M. Kotake, Asakura Shoten, (Tokyo), Vol. 13, pp. 529—533.

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