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Synthesis of 8,8-Dicyanoheptafulvene Derivatives from Several 2,5-Dioxygenated Tropones

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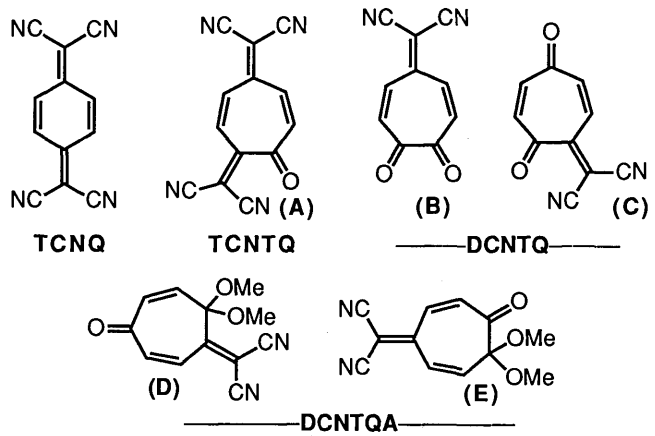
4-Acetoxy-8,8-dicyano-1-methoxyheptafulvene and 3-acetoxy-8,8-dicyano-4-methoxyheptafulvene, were synthesized with condensation of 2,5-dialkoxytropone derivatives to malononitrile. Subsequent saponification yielded 8,8-dicyano-5-hydroxy-1-methoxyheptafulvene and 8,8-dicyano-4-hydroxy-5-methoxyheptafulvene.

As 7,7,8,8-tetracyanoquinodimethane (TCNQ) is an excellent electron acceptor, its charge transfer complex formation with various electron donating compounds has been extensively investigated.[1] However, no non-benzenoid analog, such as 4,7-bis(dicyanomethylene)-2,5-cycloheptadien-1-one (**A**), 5-(dicyanomethylene)-3,6-cycloheptadiene-1,2-dione (**B**), or 2-(dicyanomethylene)-3,6-cycloheptadiene-1,5-dione (**C**), has been studied yet. Therefore, it will be worthwhile to synthesize bis(oxygenated)8,8-dicyanoheptafulvenes as their precursors. Herein, we describe the synthesis of these dicyanoheptafulvene derivatives.



(Chart 1)

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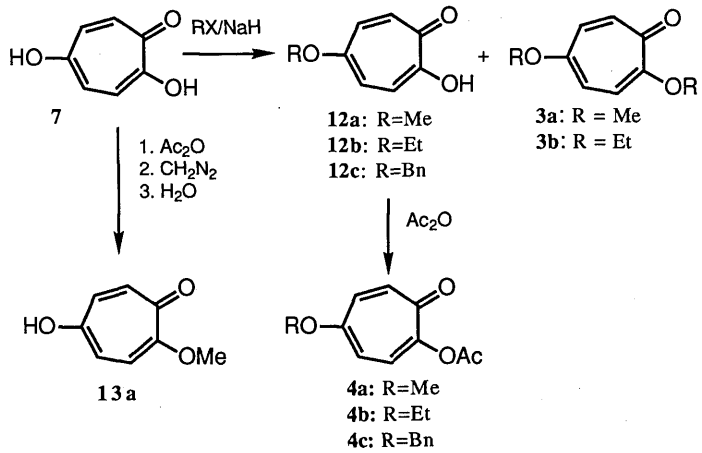
Results and discussion

Preparation of 2,5-Bis(oxygenated)tropones. Previously, Kitahara et al.[2] synthesized 8,8-dicyanoheptafulvenes (**1**)[3] by heating an acetic-anhydride solution of tropones and malononitrile (**2**). Extension of this procedure to 2,5-dialkoxytropones (**3**), 2-acetoxy-5-alkoxytropones (**4**), and/or 5-acetoxy-2-alkoxytropones (**5**), as well as 2,5-diacetoxytropone (**6**), whose preparation from 5-hydroxytropolone (**7**) would be no problem, should afford oxygenated derivatives of **1** (**8, 9, 10** and **11**). However, this should be carried out under carefully controlled conditions since they are equivalent to the intermediate compounds in the Nozoe's azulene synthesis from reactive troponoids and **2**.[4] Namely, a controlled monoalkylation of **7** gave 5-alkoxytropolones (**12**) in good yields, and exhaustive alkylation gave 2,5-dialkoxytropones (**3**).[5] Also 2-alkoxy-5-hydroxytropones (**13**) were prepared by treatment of 5-acetoxytropolone with diazoalkanes,[6] and 4,5-dialkoxytropones (**14**) were by-products of diazoalkane treatment of **7**.[7]

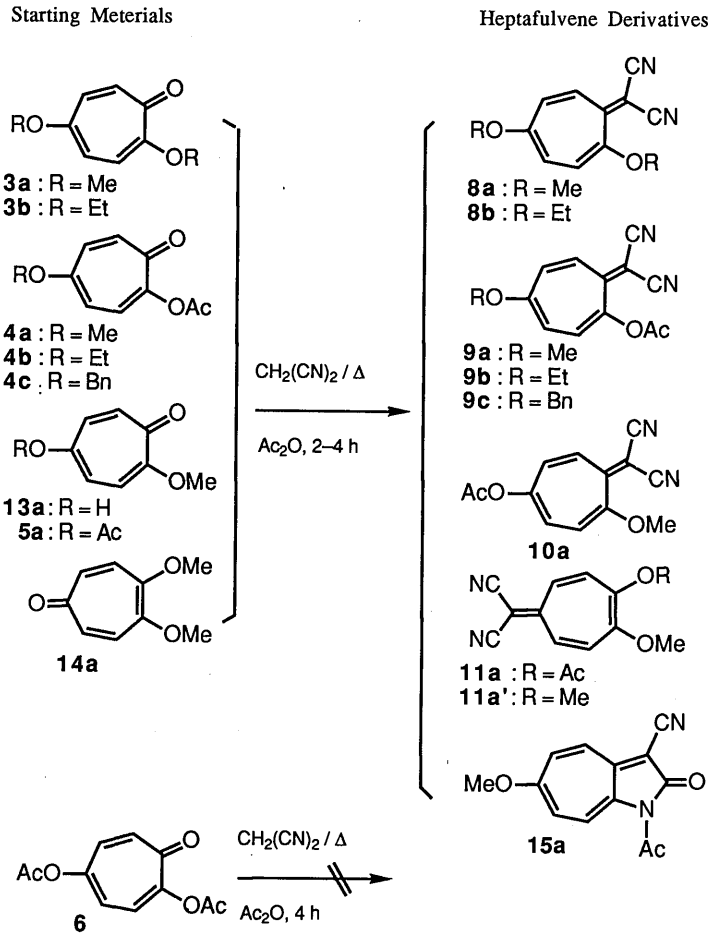


(Scheme 1)

Synthesis of 8,8-Dicyanoheptafulvene Derivatives. The treatment of **6** in acetic anhydride with **2** gave no product, resulting in a quantitative recovery of the starting material. However, heating an acetic anhydride solution of 2,5-dimethoxytropone (**3a**) and **2** at 120℃ for 4 h indeed furnished two products (**8a** and **15a**) in 57 and 12% yields, respectively.

The ^{1}H NMR spectrum of the major product (**8a**), $C_{12}H_{10}N_2O_2$, revealed four aromatic proton signals and two methoxyl signals, and the ^{13}C NMR spectrum revealed two cyano carbon signals at $\delta = 114.7$ and 116.4. An absorption band at 2200 cm^{-1} in its IR spectrum was due to $\nu_{C\equiv N}$ of a conjugated cyano group. These date were consistent to those of 8,8-dicyano-1,4-dimethoxyheptafulvene.

The molecular formula ($C_{13}H_{10}N_2O_3$) of the minor product, **15a**, indicated that an elimination of methanol occurred during the reaction. The ^{1}H NMR spectrum revealed four



(Scheme 2)

aromatic proton signals with large coupling constants (11.0-12.2 Hz), which indicated a presence of the seven-membered conjugated system, together with low-field-shifted *N*-acetyl signal at $\delta = 2.81$ and a methoxyl signal at 3.94. Its cyano group ($\delta = 113.2$ and $\nu_{C\equiv N}$ at 2210 cm^{-1}) was also conjugated in nature. Therefore, **15a** must be a cyclized product, 1-acetyl-3-cyano-6-methoxycyclohepta[*b*]pyrrol-2(1*H*)-one. Although a formation of **15a** was recognized, this prompted us to extend the reaction to other tropones.

Thus, 2,5-diethoxytropone (**3b**) was similarly treated with **2** to give corresponding 8,8-dicyano-1,4-diethoxyheptafulvene (**8b**) in 83% yield.

Also 5-hydroxy-2-methoxytropone (**13a**) gave two products (**10a** and **11a**) in 64 and 11% yields, respectively; the major product (**10a**) was identified to be 4-acetoxy-8,8-dicyano-1-methoxyheptafulvene, and the isomeric minor product (**11a**) was 3-acetoxy-8,8-dicyano-4-methoxyheptafulvene. Since **13a** should be at first acetylated under the reaction conditions, 5-acetoxy-2-methoxytropone (**5a**) must be the reacting species. Indeed, it

yielded same products (**10a**; 64% and **11a**; 15%) in similar yields.

In the case of 4,5-dimethoxytropone (**14a**),[7] a single product was formed in 33% yield. According to the spectral data, its structure was, however, not the expected dimethoxy derivative (**11a'**) but an acetoxy methoxy derivative (**10a**). Several dicyanoheptafulvene derivatives prepared from tropone derivatives by this method are compiled in Table 1, and their characteristic data employed for structure elucidations are shown in Table 2.

When **8a** was treated with acetyl trifluoroacetate in acetic anhydride[8] at 100℃ for 45 h, two products (**15a** and **16a**) were formed in 6 and 89% yields, respectively. The ^{1}H NMR spectrum of **16a** was consistent to that of 3-cyano-6-methoxy-2*H*-cyclohepta[*b*]furan-2-one.

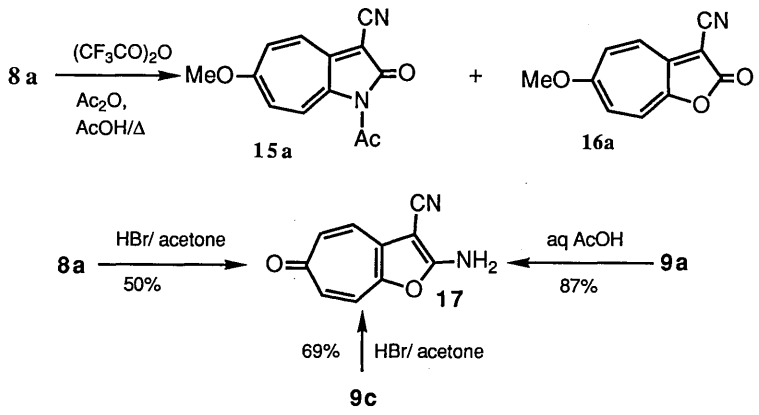
The acid hydrolysis of 8,8-dicyanoheptafulvene derivatives, **8a**, **9a** and **9c**, yielded a same product which was, however, not the desired 8,8-dicyanoheptafulvene derivative, but a

Table 1. The acetic anhydride mediated condensation of 2,5-dialkoxytropones to malononitrile at 120 ℃.

Entry	Starting Materials	Time/h	Products (yields)	
1	**3a**	4	**8a** (57%),	**15a** (12%)
2	**3b**	2	**8b** (83%)	
3	**6**	2.5	**6** (q.)	
4	**13a**	2.5	**8a** (64%),	**9a** (11%)
5	**5a**	2	**8a** (64%),	**9a** (15%)
6	**12a**	2	**9a** (62%)	
7	**12b**	2	**9b** (57%)	
8	**4b**	2	**9b** (55%)	
9	**12c**	2	**9c** (39%),	**4c** (53%)
10	**14a**	2	**10a** (33%)	

Table 2. The ^{13}C NMR Chemical Shifts of Disubstituted 8,8-Dicyanoheptafulvenes.

	1,4-Disubstituted						3,4-Disubstituted		
	8a	**8b**	**10a**	**9a**	**9b**	**9c**	**18a**	**11a**	**19a**
R1	Me	Et	Me	Ac	Ac	Ac	Me	Ac	H
R2	Me	Et	Ac	Me	Et	Bt	H	Me	Me
C-1	155.3	154.8	154.7	144.9	144.9	145.0	151.6	134.1	134.3
C-2	114.7	115.3	111.2	107.7	108.1	108.9	119.4	128.5	130.2
C-3	109.8	110.9	125.3	133.0	132.9	132.9	117.3	142.8	152.1
C-4	153.7	153.2	150.8	155.0	155.0	155.0	155.3	156.5	156.1
C-5	132.1	132.0	131.0	135.0	135.0	135.0	133.0	127.9	126.6
C-6	133.4	133.4	134.7	134.9	135.0	135.0	133.2	136.4	131.0
C-7	161.4	160.9	159.0	165.7	165.2	164.7	162.2	160.0	157.5
C-8	65.3	66.2	68.6	65.3	65.5	65.5	56.8	66.9	53.4
C-N	116.4	116.8	115.5	115.8	115.7	115.7	117.3	115.0	117.8
	117.1	117.4	116.1	116.0	116.0	116.0	117.3	115.1	117.8



(Scheme 3)

a cyclized product, 2-amino-3-cyano-6*H*-cyclohepta[*b*]furan-6-one (**17**), $C_{10}H_6N_2O_2$.

On the other hand, the acid hydrolysis of **11a** gave a complex mixture.

As the acid hydrolysis gave a cyclohepta[*b*]buran-6-one derivative (**17**), hydrolysis under basic conditions was carried out in a hope of obtaining free hydroxy derivatives; the desired **18a** was formed from **10a** in 60% yield, and **19a** from **11a** in 54% yield.

Conclusion. As described above, several heptafulvene derivatives from 5- hydroxytropolone were prepared. However, these heptafulvenes carrying oxygen functions at neighboring carbons tend to cyclize to cyclohepta[*b*]furanones and cyclohepta[*b*]pyrrolones. In order to transform these heptafulvenes into tropoquinone dicyanomethide derivatives, it must be converted these alkoxy groups into hydroxy derivatives without heteroazulene cyclization. The results will be reported in future.

Experimental

The elemental analyses were carried out by Miss. T. Mizoguchi and Mrs. M. Miyazawa, of Institute of Advanced Material Study, Kyushu University. The NMR spectra were measured with a JEOL GSX 270 H model spectrometer in $CDCl_3$ solution, unless otherwise specified, and the chemical shifts were expressed in δ unit. The mass spectra were measured with a JEOL 01SG-2 spectrometer. The IR spectra were taken as KBr disk using a Jasco IR-A 102 spectrometer. The UV spectra were measured with a Hitachi U-3200 spectrophotometer.

General Procedure for Alkylation of 5-Hydroxytropolone. a) (Exhaustive Alkylation). To an HMPA solution (10 cm^3) of **7** (1.00 g), NaH (50%, 800 mg) was added under an N_2 atmosphere at room temperature. Then, while being stirred for 1 h, alkyl halide (2.3 mol eq) was added to the mixture and stirred at 60℃ for another 3 h. The mixture was poured into water, acidified with 0.1 N HCl, extracted with AcOEt, and dried over anhydrous $MgSO_4$. After removing the solvents in vacuo, the residue was chromatographed on silica-gel column to give 2,5-dialkoxytropones (**3**).

2,5-Diethoxytropone (3b): Colorless crystals, mp 48-50℃. Found: C, 68.17; H, 7.18%. Calcd for $C_{11}H_{14}O_3$: C, 68.02; H, 7.27%. ^{1}H NMR δ =1.42 (3H, t, J=7.0 Hz), 1.49 (3H, t, J=7.0 Hz), 3.96 (2H, q, J=7.0 Hz), 4.08 (2H, q, J=7.0 Hz), 6.31 (1H, ddd, J =10.9, 2.8, 0.7 Hz), 6.75 (1H, d, J=10.9 Hz), 7.07 (1H, dd, J=13.2, 2.8 Hz), and 7.19 (1H, dd, J=13.2, 0.7 Hz). ^{13}C NMR δ =14.6 (2C), 64.0, 64.7, 108.4, 115.2, 132.8, 137.4, 158.8, 159.3, and 179.6. IR ν : 3075, 2980, 2920, 2870, 1630, 1570, 1510, 1440, 1390, 1360, 1275, 1245, 1220, 1200, 1110, 1035, 855, 840, and 700 cm^{-1}. MS m/z (%) 194 (91, M^+), 179 (27), 151 (32), 150 (25), 149 (74), 138 (39), 137 (20), 122 (30), 121 (45), 110 (100), 109 (34), 94 (21), 81 (33), 65 (27), 39 (22), 29 (38), and 27 (56). UV λ_{max}^{MeOH} =230 mm (ε =23900), 252 (8400, sh), 329 (11800), 349 (10300, sh), 362 (9800, sh), and 381 (7000, sh).

b) (Controlled Alkylation). To an HMPA solution (10 cm^3) of **7** (1.50 g), NaH (50%, 550 mg) was added under an N_2 atmosphere at room temperature. While being stirred for 30 min, alkyl halide (1.2 mol eq) was added to the mixture and stirred at 60℃ for another 1 h. The mixture was then similarly treated as above to give the 5-alkoxytropolones (**12**), whose acetylation with Ac_2O afforded quantitative amounts of **3**.

5-Ethoxytropolone (12b): Pale yellow needles, mp 136.5-137.5℃ (lit.[10] mp 134-135℃),. ^{1}H NMR δ =1.43 (3H, t, J=7.0 Hz), 3.99 (2H, q, J=7.0 Hz), 6.95 (2H, dm, J= 12 Hz), and 7.29 (2H, dm, J=12 Hz). ^{13}C NMR δ =14.6, 64.4, 123.7 (2C), 124.4 (2C), 159.2, and 168.2 (2C). IR ν : 3230, 1600, 1540, 1445, 1420, 1265, 1190, 1115, 1030, and 760 cm^{-1}. MS m/z (%) 166 (82, M^+), 138 (36), 110 (72), 44 (49), and 28 (100). UV λ_{max}^{MeOH}=233 nm (ε =14900), 338 (6900), 365 (3800, sh), 385 (3500), and 415 (1800, sh).

2-Acetoxy-5-ethoxytropone (4b): Colorless prisms, mp 101-103℃. Found: C, 63.60; H, 5.89%. Calcd for $C_{11}H_{12}O_4$: C, 63.45; H, 5.81%. ^{1}H NMR δ =1.44 (3H, t, J=7.0 Hz), 2.32 (3H, s), 3.99 (2H, q, J=7.0 Hz), 6.6 (2H, br.s), and 7.16 (2H, d, J=11.8 Hz). ^{13}C NMR δ =14.2, 20.6, 64.3, 162.8 (C-5) and 168.5, where signals of C-1, 2, 3, 4, 6, and 7 were not observable.[11] IR ν : 2975, 1750, 1570, 1520, 1390, 1365, 1255, 1200, 1170, 1075, 1025, and 860 cm^{-1}. MS m/z (%) 208 (9, M^+), 166 (100), 138 (77), 110 (67), 43 (40), and 28 (73). UV λ_{max}^{MeOH}=225 nm (ε =23300), 253 (9400, sh), 262 (3500, sh), 299 (5600, sh), 332 (13900), and 341 (12700, sh).

5-Benzyloxytropolone (12c): Colorless crystals, mp 151.5-153.5℃ . Found: C, 73.48; H, 5.35%. Calcd for $C_{14}H_{12}O_3$: $C_7$3.67; H, 5.30%. ^{1}H NMR δ =5.04 (2H, s), 7.05 (2H, dm, J=12 Hz), 7.29 (2H, dm, J=12 Hz), and 7.3-7.45 (5H, m). ^{13}C NMR δ = 70.9, 124.1 (2C), 124.3 (2C), 127.5 (2C), 128.5, 128.8 (2C), 135.5, 158.8, and 168.4 (2C). IR ν : 3250, 1605, 1545, 1455, 1430, 1260, 1210, 1190, 1025, 860, and 730 cm^{-1}. MS m/z (%) 229 (7, M^+ + 1), and 91 (100). UV λ_{max}^{MeOH} = 234 nm (ε = 26200), 332 (12400, sh), 340 (13400), 385 (6600), and 417 (2400, sh).

2-Acetoxy-5-benzyloxytropone (4c): Colorless crystals, mp 121-122℃. Found: C, 71.36; H, 5.27%. Calcd for $C_{16}H_{14}O_4$: C, 71.00; H, 5.22%. ^{1}H NMR δ =2.32 (3H, s), 5.03 (2H, s), 6.7 (2H, br s), 7.16 (2H, d, J=11.7 Hz), and 7.35-7.45 (5H, m). ^{13}C NMR δ = 20.7, 70.7, 127.6 (2C), 128.7, 128.9 (2C), 134.9, 160.6, and 168.6, and other broadened signals of C-1, 2, 3, 4, 6, and 7.[10] IR ν : 1765, 1590, 1530, 1370, 1245, 1190, 1165, 1070, 985, 850, and 745 cm^{-1}. MS m/z (%) 229 (15), 228 (88, M^+), 92 (35), 91

(100), 65 (37), and 43 (66). UV λ_{max}^{MeOH} = 222 nm (ε = 24300), 251 (8200, sh), 332 (14600), and 341 (13300, sh).

Synthesis of 8,8-Dicyanoheptafulvenes (General Procedure). An Ac_2O solution (15 cm^3) of tropones (ca. 1.0 g) and **2** (ca. 1.2 g, 3 mol eq) was stirred at 120℃ for 2 to 4 h. After removing the solvents in vacuo, the residue was chromatographed on a silica-gel column to give the products:

8a: Red needles, mp 222-224℃. Found: C, 67.33; H, 4.77; N, 13.17%. Calcd for $C_{12}H_{10}N_2O_2$: C, 67.28; H, 4.71;N, 13.08%. ^{1}H NMR δ = 3.81 (3H, s), 3.92 (3H, d, J = 0.7 Hz), 6.34 (1H, dd, J = 11.0, 2.9 Hz), 6.52 (1H, br d, J = 11.0 Hz), 6.91 (1H, dd, J = 12.8, 2.9 Hz), and 7.52 (1H, d, J = 12.8 Hz). IR ν : 2200, 1510, 1450, 1400, 1365, 1310, 1270, 1220, 1190, 970, 830, and 740 cm^{-1}. MS m/z (%) 214 (55, M^+), 174 (100), 171 (92), 146 (41), 141 (44), 128 (43), 116 (48), 114 (38), 102 (34), 101 (36), 89 (25), 76 (30), 75 (33), 63 (23), 51 (26), 50 (24), and 39 (24). UV λ_{max}^{MeOH} = 218 nm (ε = 12800, sh), 248 (13700), 268 (9100, sh), 280 (12100), 292 (12700), 446 (26100), and 459 (24300, sh).

15a: Reddish yellow crystals, mp 237-239℃. Found: C, 64.20; H, 4.33; N, 11.54%. Calcd for $C_{13}H_{10}N_2O_3$: C, 64.46; H, 4.16; N, 11.56%. ^{1}H NMR δ = 2.81 (3H, s), 3.94 (3H, s), 6.81 (1H, dd, J = 11.0, 2.9 Hz), 7.34 (1H, dd, J = 12.1, 2.9 Hz), 7.79 (1H, d, J = 12.1 Hz), and 8.96 (1H, d, J = 11.0 Hz). ^{13}C NMR δ = 27.7, 56.4, 86.3, 113.2, 113.6, 124.9, 129.6, 133.9, 136.7, 149.7, 164.5, 164.8, and 173.1. IR ν : 2210, 1710, 1590, 1540, 1510, 1470, 1405, 1365, 1290, 1250, 1210, 1130, 985, 850, and 700 cm^{-1}. MS m/z (%) 242 (12, M^+), 201 (14), 200 (100), 185 (25), 157 (62), 102 (15), and 43 (34). UV λ_{max}^{MeOH} = 217 nm (ε = 16700), 254 (11700), 279 (20500), 286 (20100), 302 (14300, sh), 415 (17000, sh), and 433 (21400).

8b: Orange needles, mp 209-211℃. Found: C, 69.55; H, 5.80; N, 11.71%. Calcd for $C_{14}H_{14}N_2O_2$: C, 69.41; H, 5.82; N, 11.56%. ^{1}H NMR δ = 1.43 (3H, t, J = 7.0 Hz), 1.57 (3H, t, J = 7.0 Hz), 3.98 (2H, q, J = 7.0 Hz), 4.16 (2H, q, J = 7.0 Hz), 6.32 (1H, dd, J = 11.1, 3.0 Hz), 6.53 (1H, d, J = 11.1 Hz), 6.90 (1H, dd, J = 13.0, 3.0 Hz), and 7.52 (1H, d, J = 13.0 Hz). IR ν : 2200, 1515, 1455, 1405, 1375, 1320, 1295, 1265, 1220, 1110, 1015, and 880 cm^{-1}. MS m/z (%) 242 (21, M^+), 199 (17), 186 (77), 158 (29), 157 (38), 131 (18), 130 (18), 129 (26), 103 (16), 102 (24), 76 (17), 43 (20), 41 (20), 29 (74), and 27 (100). UV λ_{max}^{MeOH} = 249 nm (ε = 14100), 281 (12300), 293 (13600), 449 (26700), and 459 (25600, sh).

10a: Red needles, mp 196-198℃. Found: C, 64.38; H, 4.30; N, 11.54%. Calcd for $C_{13}H_{10}N_2O_3$: C, 64.46; H, 4.16; N, 11.56%. ^{1}H NMR δ = 2.29 (3H, s), 3.99 (3H, s), 6.40 (1H, d, J = 10.6 Hz), 6.75 (1H, dd, J = 10.6, 2.6 Hz), 6.82 (1H, dd, J = 12.8, 2.6 Hz), and 7.48 (1H, d, J = 12.8 Hz). IR ν : 2205, 1765, 1495, 1455, 1400, 1365, 1315, 1285, 1260, 1195, 1160, 1010, 980, 890, 840, and 820 cm^{-1}. MS m/z (%) 242 (12, M^+), 201 (13), 200 (100), 185 (20), 157 (30), and 43 (69). UV λ_{max}^{MeOH} = 244 nm (ε = 12500), 269 (16000, sh), 278 (16400), 412 (20400, sh), and 425 (22200).

11a: Reddish orange crystals, mp 190-192℃. Found: C, 64.31; H, 4.20, N; 11.27%. Calcd for $C_{13}H_{10}N_2O_3$: C, 64.46; H, 4.16; N, 11.56%. ^{1}H NMR δ = 2.30 (3H, s), 3.94 (3H, s), 6.84 (1H, d, J = 12.5 Hz), 7.09 (1H, d, J = 13.0 Hz), 7.15 (1H, dd, J = 12.5, 2.6 Hz), and 7.47 (1H, dd, J = 13.0, 2.6 Hz). IR ν : 2200, 1765, 1490, 1405, 1270, 1235, 1185, 1165,

1100, 875, and 685 cm^{-1}. MS *m/z* (%) 242 (9, M^+), 200 (50), 160 (48), 157 (14), 129 (13), 102 (18), 101 (10), 76 (11), 75 (13), and 43 (100). UV λ_{max}^{MeOH} = 235 nm (ε = 10100), 251 (10000), 291 (5100, sh), 415 (27800, sh), and 426 (29100).

9a: Reddish orange needles, mp 172-174℃. Found: C, 64.63; H, 4.47, N; 11.58%. Calcd for $C_{13}H_{10}N_2O_3$: C, 64.46; H, 4.16; N, 11.56%. ^{1}N NMR δ = 2.40 (3H, s), 3.86 (3H, s), 6.20 (1H, dd J = 10.6, 3.3 Hz), 6.83 (1H, d J = 10.6 Hz), 6.91 (1H, dd, J = 13.2, 3.3 Hz), and 7.54 (1H, d, J = 13.2 Hz). IR ν : 2200, 1765, 1525, 1495, 1450, 1400, 1370, 1360, 1315, 1290, 1245, 1200, 1150, 1090, 1005, 870, 840, and 825 cm^{-1}. MS *m/z* (%) 242 (18, M^+), 201 (13), 200 (100), 185 (11), 157 (17), and 43 (43). UV λ_{max}^{MeOH} = 240 mm (ε = 13400), 282 (8700), 289 (7600, sh), 400 (19600, sh), and 422 (27300).

9b: Orange needles, mp 150℃ (decomp). Found: C, 65.57; H, 4.81; N, 11.03%. Calcd for $C_{14}H_{12}N_2O_3$: C, 65.62; H, 4.72; N, 10.93%. ^{1}H NMR δ = 1.46 (3H, t, J = 7.0 Hz), 2.40 (3H, s), 4.04 (2H, q, J = 7.0 Hz), 6.17 (1H, dd, J = 10.9, 3.0 Hz), 6.80 (1H, d, J = 10.9 Hz), 6.90 (1H, dd, J = 13.2, 3.0 Hz), and 7.54 (1H, d, J = 13.2 Hz). IR ν : 2200, 1755, 1530, 1490, 1450, 1365, 1290, 1240, 1200, 1155, 1020, 870, and 840 cm^{-1}. MS *m/z* (%) 256 (17, M^+), 214 (50), 186 (100), 43 (63). UV λ_{max}^{MeOH} = 240 mm (ε = 14400), 283 (9600), 291 (8100, sh), and 425 (27700).

9c: Red crystals, mp 122-124℃. Found: C, 71.90; H, 4.60; N, 8.82%. Calcd for $C_{19}H_{14}N_2O_3$: C, 71.69; H, 4.43; N, 8.80%. ^{1}H NMR δ = 2.39 (3H, s), 5.06 (2H, s), 6.28 (1H, dd, J = 11.0, 2.9 Hz), 6.80 (1H, d, J = 11.0 Hz), 6.96 (1H, dd, J = 13.2, 2.9 Hz), 7.35-7.45 (5H, m), and 7.54 (1H, d, J = 13.2 Hz). IR ν : 2200, 1780, 1520, 1490, 1445, 1400, 1365, 1315, 1285, 1230, 1190, 1145, 980, 840, and 760 cm^{-1}. MS *m/z* (%) 318 (3, M^+), 276 (10), 91 (100), and 43 (17). UV λ_{max}^{MeOH} = 240 nm (ε = 13800), 283 (10000), 291 (8500, sh), 329 (2100), and 424 (25300).

Attempted Condensation of 2,5-Diacetoxytropone (6) with 2. An Ac_2O solution (5 cm^3) of **6** (200 mg) and **2** (200 mg) was stirred at 120℃ for 2.5 h. After removing the solvents in vacuo, the residue was chromatographed on a silica-gel column to recover **6** (200 mg).

Condensation of 4,5-Diacetoxytropone (14a) with 2 to 10a. An Ac_2O solution (2 cm^3) of **14a** (50 mg) and **2** (62 mg) was strred at 120℃ for 1 h. After removing the solvents in vacuo, the residue was chromatographed on a silica-gel column to give **10a** (25 mg, 33%).

An ATA-Treatment of 8a. An ATA solution [$(CF_3CO)_2O$ (242 mg), AcOH (0.7 cm^3), Ac_2O (10 cm^3)] of **8a** (40 mg) was heated in sealed tube at 100℃ for 45 h. After removing the solvents, the residue was chromatographed on silica-gel column to give **15a** (3 mg, 6%.) and **16a** [yellow crystals, mp 221-222℃, 34 mg, 89%. Found: *m/z*, 201.0432 (M^+). Calcd for $C_{11}H_7NO_3$: 201.0425. ^{1}H NMR δ = 3.94 (3H, s), 6.82 (1H, dd, J = 10.6, 2.9 Hz), 7.43 (1H, dd, J = 12.1, 2.9 Hz), 7.44 (1H, d, J = 10.6 Hz), and 7.76 (1H, d, J = 12.1 Hz). ^{1}H NMR (DMSO-d_6) δ = 3.96 (3H, s), 7.31 (1H, dd, J = 11.0, 2.9 Hz), 7.67 (1H, dd, J = 12.1, 2.9 Hz), 7.87 (1H, d, J = 11.0 Hz), and 7.93 (1H, d, J = 12.1 Hz). ^{13}C NMR (DMSO-d_6) δ = 57.0, 76.3, 113.6, 115.6, 121.8, 129.0, 135.4, 151.1, 151.3, 165.0, and 165.3. IR ν : 2205, 1740, 1615, 1540, 1505, 1450, 1360, 1315, 1250, 1190, 975, and 695 cm^{-1}. MS *m/z* (%) 202 (12), 201 (100, M^+), 186 (10), 158 (25), 145 (14), 130 (12), 102

(15), and 76 (11). UV λ_{max}^{MeOH} = 206 nm (ε = 15600), 236 (19800), 267 (12600, sh), 282 (14800), 409 (22100, sh), and 428 (27100)].

An Acid-Treatment of 8a to 2-Amino-3-cyano-6*H*-cyclohepta[*b*]furan-6-one (17). An acetone-aq HBr solution (1:1, 10 cm^3) of **8a** (50 mg) was refluxed for 3 h. The mixture was neutralized with aq $NaHCO_3$ and the precipitates were collected by filtration to give **17** [orange crystals, mp > 300℃, 19 mg, 50%, Found: C, 64.17; H, 3.52; N, 14.95%. Calcd for $C_{10}H_6N_2O_2$: C, 64.52; H, 3.25; N, 15.05%. ^{1}H NMR (DMSO-d_6) δ = 6.63 (1H, dd, J = 12.1, 2.6 Hz), 6.95 (1H, dd, J = 12.1, 2.6 Hz), 7.32 (1H, d, J = 12.1 Hz), 7.53 (1H, d, J = 12.1 Hz), and 8.61 (2H, s, -N$\underline{H_2}$). ^{13}C NMR (DMSO-d_6) δ = 67.0, 113.4, 124.8, 127.3, 130.9, 131.1, 139.3, 145.4, 164.3, and 184.6. IR ν: 3355, 3310, 2920, 2215, 1680, 1575, 1510, 1450, 1320, 1225, 1160, and 855 cm^{-1}. MS m/z (%) 186 (58, M$^+$), 159 (11), 158 (100), 115 (17), 103 (34), 76 (19), and 28 (11). UV λ_{max}^{MeOH} = 233 nm (ε = 11800, sh), 240 (13200), 258 (11900), 294 (5400, sh), 366 (13600, sh), 383 (15200), and 409 (9300, sh)].

An Acid-Hydrolysis of 9a to 17. An aq HOAc (10 cm^3) solution of **9a** (180 mg) was refluxed for 14 h. The precipitates were collected by filtration to give **17** (120 mg, 87%).

An Acid-Hydrolysis of 9c to 17. An acetone-aq HBr solution (10:3, 13 cm^3) of **9c** (576 mg) was refluxed for 3 h. The mixture was neutralized with aq $NaHCO_3$ and the precipitates were collected by filtration to give **17** (234 mg, 69%).

Saponification of 10a to 8,8-Dicyano-4-hydroxy-1-methoxyheptafulvene (18a). An MeOH solution (20 cm^3) containing **10a** (1.50 g) and NaOH (200 mg) was refluxed for 1 h. The mixture was then acidified with dil H_2SO_4. The precipitates were collected by filtration and washed with water and $CHCl_3$ to give **18a** [red powder, mp 250℃ (decomp), 859 mg, 69%. Found: C, 65.70; H, 4.26; N, 13.95%. Calcd for $C_{11}H_8N_2O_2$: C, 66.00; H, 4.03; N, 13.99%. ^{1}H NMR (DMSO-d_6) δ = 3.89 (3H, s), 6.77 (1H, dd, J = 11.4, 2.9 Hz), 7.08 (1H, d, J = 11.4 Hz), 7.20 (1H, dd, J = 12.8, 2.9 Hz), and 7.59 (1H, d, J = 12.8 Hz). ^{13}C NMR (DMSO-d_6) δ = 55.9, 56.8, 117.3 (3C), 119.4, 133.0, 133.2, 151.6, 155.3, and 162.2. IR ν: 3500-2400, 2190, 1510, 1435, 1380, 1305, 1260, 1225, 1190, 1110, 985, 940, 845, 825, and 755 cm^{-1}. MS m/z (%) 200 (100, M$^+$), 185 (15), 172 (50), 160 (43), 157 (54), 145 (16), 132 (36), 129 (28), 103 (16), 102 (33), and 76 (22). UV λ_{max}^{MeOH} = 250 (ε = 12800), 286 (sh, 9500), 294 (10100), 321 (sh, 2700), and 461 (27100)].

Saponification of 11a to 8,8-Dicyano-3-hydroxy-4-methoxyheptafulvene (19a). An MeOH solution (15 cm^3) of **11a** (971 mg) and NaOH (160 mg) was refluxed for 1 h. The mixture was then acidified with dil H_2SO_4. The resultant precipitates were collected by filtration and washed with water and $CHCl_3$ to give **19a** [red powder, mp 240℃ (decomp), 430 mg, 54%. Found: C, 65.90; H, 4.20; N, 13.89%. Calcd for $C_{11}H_8N_2O_2$: C, 66.00; H, 4.03; N, 13.99%. ^{1}H NMR (DMSO-d_6) δ = 3.94 (3H, s), 7.22 (1H, dd, J = 12.5, 2.2 Hz), 7.36 (1H, dd, J = 12.5, 2.2 Hz), 7.43 (1H, d, J = 12.5 Hz), and 7.69 (1H, d, J = 12.5 Hz). ^{13}C NMR (DMSO-d_6) δ = 53.4, 57.4, 117.8 (2C), 126.6, 130.2, 131.0 134.3, 152.1, 156.1, and 157.5. IR ν: 3600-2400, 2195, 1650, 1480, 1375, 1260, 1220, 1170, 1110, 985, 965, 875, 845, 825, and 690 cm^{-1}. MS m/z (%) 200 (59, M$^+$), 185 (38), 158 (12), 157 (100), 102 (23), 76 (14), 75 (14), and 51 (11). UV λ_{max}^{MeOH} = 223 (ε = 25100), 250 (16700, sh), 306 (5800), 320 (5300, sh), 416 (22600, sh), and 444 (27100)].

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