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Palladium-Catalyzed Vinylation of Haloazulenes and Halotropolones with Olefins. Utility of the Heck Reaction in the Conjugated Carbon Chain Preparation[1,2]

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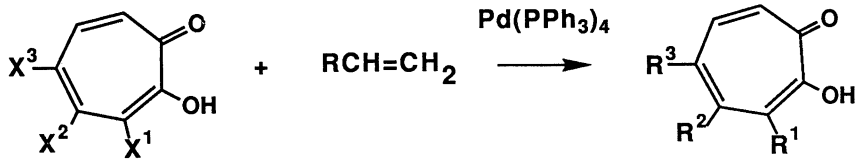
The reactions of 3-iodotropolone with styrenes (styrene, *p*-methoxystyrene, and 2-vinylpyridine), methyl acrylate, and allylic compounds (methyl 3-butenoate, 3-butenenitrile, 1-allyl-3,4-dimethoxybenzene, and 1-allyl-3,4-methylenedioxybenzene) were carried out, according to the modified Heck's procedure, to give 3-styryl-, 3-(2-carboxyvinyl)-, and 3-(3-substituted 1-propenyl)tropolones, respectively. Similarly, 4-bromo- or 5-bromotropolone was made to react with these olefins to yield 4-styryltropolone or the corresponding 5-(2-substituted vinyl)- and 5-(3-substituted 1-propenyl)tropolones. Substitution of 2-chlorotropone by styrenes produced 2-styryltropones. Extension of the vinylation to 2-amino-6-bromoazulenes, ethyl 3-bromo-1-azulenecarboxylate, and diethyl 2-chloro-1,3-azulenedicarboxylate resulted in a similar substitution.

Many investigations have been undertaken on the chemical and spectroscopic properties of the conjugated or cross-conjugated compounds including azulenes and tropolones. For example, the absorption spectra of azulenes are known to be strongly influenced by the degree of conjugation of the carbon chain substituents as well as their positions.[3d] Such a study needs the synthetic methods for elongation or introduction of a conjugated carbon chain to these compounds. Although many efforts have been devoted, the hitherto-known methods making a carbon–carbon double bond on azulene nuclei or tropolone rings are limited.[3] However, the recent development of the carbon–carbon coupling reactions by transition metal complexes is providing us short-step syntheses of new nonbenzenoid aromatic compounds by coupling the common azulenes or tropolones with easily accessible reagents. Since we reported the palladium-catalyzed vinylation of halotropolones and halotropones about a decade ago,[4] the palladium-catalyzed cross-coupling reactions such as carbonylative coupling[5] as well as alkenyl, alkyl, and aryl coupling with organostannanes,[6] aryl coupling with organoboranes,[7] and aryl coupling with organozinc compounds[8] have been published successively. Nickel-assisted coupling of halotropones or haloazulene to synthesize bitropones and bitropolones[9a,c] or biazulene[9b] has also reported. The benzidine-type rearrangement of 2-(2-arylhydrazino)tropones to 2-amino-5-(4-aminoaryl)tropones,[10] and the base-catalyzed[11] or homolytic rearrangement[12] of 2-benzyloxytropones to 3-arylmethyltropolones have recently been reported as another category of carbon–carbon bond formation. Extension of the metal-assisted or catalyzed coupling reactions to the azulene chemistry is still unsatisfactory except for the copper-promoted coupling of haloazulenes and acetylene moieties.[13] Application of the Heck's vinylation to halotropolones and haloazulenes aiming to conjugated carbon substituents seems promising, because the halogen atoms of easily available halotropolones or haloazulenes are replaced regioselectively by the vinyl groups of commercially available olefins to give a variety of substituted vinyl compounds in one step under mild conditions. In this paper, we describe the details of the vinylic substitution of halotropolones with various olefins catalyzed by palladium complexes and its extension to haloazulenes.

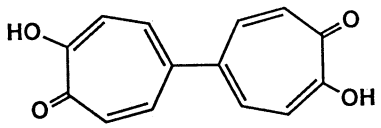
Results and Discussion

The reactions of 3-iodotropolone **1a** with styrene, *p*-methoxystyrene, 2-vinylpyridine, and methyl acrylate were carried out in sealed tubes by heating the THF solutions of the mixtures in the presence of triethylamine and tetrakis(triphenylphosphine)palladium, $Pd(PPh_3)_4$. The change of the reaction products to their sodium salts to remove the catalyst and excess base, and the subsequent acidification gave 3-styryl- **2a**, 3-[2-(*p*-methoxyphenyl)vinyl]- **2b**, 3-[2-(2-pyridyl)-vinyl]tropolone **2c**, and 3-(2-carboxylvinyl)tropolone **2d**, respectively, in moderate yields. Methyl 3-butenoate and other allylic compounds were made to react similarly to produce the corresponding 3-(3-substituted 1-propenyl)tropolones **2e—2h**, as listed in Table 1. The allylic products **2e—2f** having electron-withdrawing groups were the mixtures of allylic double bond isomers from their NMR spectra. An allylic isomerization appears to have produced the thermodynamically stable products during the vinylation as described by Heck[14] or during the treatment of the products with alkaline solutions. An extension of the reaction to 4-bromotropolone **1b** afforded 4-styryltropolone **2i** in the same procedure. All of the olefins used in the reaction of **1a** could be applied to the reaction with 5-bromotropolone **1c**, which produced 5-(2-substituted vinyl)tropolones **2j—2m** and 5-(3-substituted 1-propenyl)tropolones **2n—2o** in good yields. Nozoe et al. proposed and partially succeeded in the synthetic pathway directed toward colchicine, a tricyclic alkaloid including tropolone ring, which consisted of intra-



1a: X^1=I, X^2=X^3=H
b: X^2=Br, X^1=X^3=H
c: X^3=Br, X^1=X^2=H
d: X^3=I, X^1=X^2=H
e: X^3=Cl, X^1=X^2=H
4: X^2=Ph, X^3=Br, X^1=H

2a: R^1=PhCH=CH, R^2=R^3=H
b: R^1=p-$MeOC_6H_4CH$=CH, R^2=R^3=H
c: R^1=2-PyCH=CH, R^2=R^3=H
d: R^1=HO_2CCH=CH, R^2=R^3=H
e: R^1=HO_2CCH_2CH=CH, R^2=R^3=H
f: R^1=$NCCH_2CH$=CH, R^2=R^3=H
g: R^1=3,4-$(MeO)_2C_6H_3CH_2CH$=CH, R^2=R^3=H
h: R^1=3,4-$(CH_2O_2)C_6H_3CH_2CH$=CH, R^2=R^3=H
i: R^2=PhCH=CH, R^1=R^3=H
j: R^3=PhCH=CH, R^1=R^2=H
k: R^3=p-$MeOC_6H_4CH$=CH, R^1=R^2=H
l: R^3=2-PyCH=CH, R^1=R^2=H
m: R^3=HO_2CCH=CH, R^1=R^2=H
n: R^3=3,4-$(MeO)_2C_6H_3CH_2CH$=CH, R^1=R^2=H
o: R^3=3,4-$(CH_2O_2)C_6H_3CH_2CH$=CH, R^1=R^2=H
5a: R^2=Ph, R^3=PhCH=CH, R^1=H
b: R^2=Ph, R^3=HO_2CCH=CH, R_1=H



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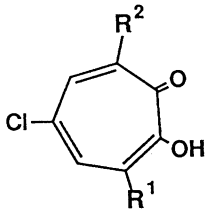
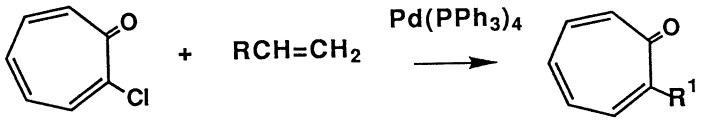


6: R^1=R^2=Br
7: R^1=R^2=PhCH=CH



8

9a: R^1=PhCH=CH
b: R^1=p-$MeOC_6H_4CH$=CH
c: R^1=2-PyCH=CH

Scheme 1.

molecular cyclization of 4-(3-arylpropyl)tropolone derivatives.[15] Then, 3-substituted tropolones **2g** and **2h** and 5-substituted products **2n** and **2o** are regarded as the model compounds approaching to the synthetic precursor for colchicine.

Although aryl iodides are usually more reactive than the corresponding aryl bromides,[14] the yields of **2a**—**2h** from 3-iodotropolone **1a** are lower than those of **2j**—**2o** from 5-bromotropolone **1c**. Surprisingly, the reaction of 5-iodotropolone **1d** with styrene or *p*-methoxystyrene gave mainly unexpected bitropolone **3**, accompanied by a small amount of **2j** as shown in

Table 1. Vinylic Substitution of Halotropolones (**1**, **4**, **6**), and 2-Chlorotropone **8**[a]

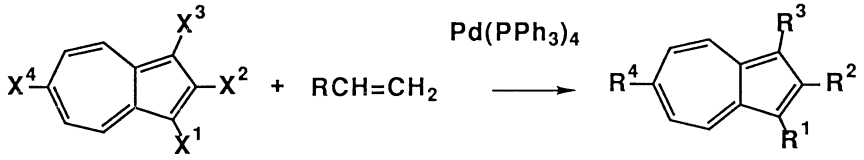
Entry	Halotropolone	Olefin	Product	Yield (%)[b]
1	**1a**	Styrene	**2a**	(39)
2	**1a**	*p*-Methoxystyrene	**2b**	(51)
3	**1a**	2-Vinylpyridine	**2c**	(43)
4	**1a**	Methyl acrylate	**2d**	(50)
5	**1a**	Methyl 3-butenoate[c]	**2e**	(51)
6	**1a**	3-Butenenitrile[d]	**2f**	(36)
7	**1a**	1-Allyl-3,4-dimethoxybenzene	**2g**	(67)
8	**1a**	1-Allyl-3,4-methylenedioxybenzene	**2h**	(34)
9	**1b**	Styrene	**2i**	(33)
10	**1c**	Styrene	**2j**	(83)
11	**1c**	Styrene	**2j**	(75)[e]
12	**1c**	Styrene	**2j**	(83)[f]
13	**1c**	Styrene	**2j**	(69)[g]
14	**1c**	Styrene	**2j**	(59)[h]
15	**1c**	*p*-Methoxystyrene	**2k**	(65)
16	**1c**	2-Vinylpyridine	**2l**	(80)
17	**1c**	Methyl acrylate	**2m**	(70)
18	**1c**	1-Allyl-3,4-dimethoxybenzene	**2n**	(55)
19	**1c**	1-Allyl-3,4-methylenedioxybenzene	**2o**	(83)
20	**1d**	Styrene	**2j**	(9)
			3	(44)
21	**1d**	*p*-Methoxystyrene	**2j**	(5)
			3	(66)
22	**4**	Styrene	**5a**	(24)
23	**4**	Methyl acrylate	**5b**	(18)
24	**6**	Styrene	**7**	(26)
25	**8**	Styrene	**9a**	(25)
26	**8**	*p*-Methoxystyrene	**9b**	(49)
27	**8**	2-Vinylpyridine	**9c**	(36)[i]

a) Carried out by heating the mixture of halotropolone (2 mmol), olefin (6 mmol), triethylamine (0.7 cm^3), and $Pd(PPh_3)_4$ (0.1 mmol) in THF (10 cm^3) at 100—110 °C for 18—20 h. b) Isolated yields based on halotropolones and 2-chlorotropone. c) A 1:1 mixture of allylic double bond isomers. d) A mixture of 3-(3-cyano-1-propenyl)- and 3-(3-cyano-2-propenyl)tropolones by a ratio of 1:2. e) $Pd_2(dba)_3 \cdot CHCl_3$ (0.1 mmol) was used as the catalyst. f) The mixture of $Pd_2(dba)_3 \cdot CHCl_3$ (0.1 mmol) and PPh_3 (0.4 mmol) as the catalyst. g) The mixture of $Pd_2Cl_4(PPh_3)_2$[18] (0.1 mmol) and PPh_3 (0.4 mmol) was used as the catalyst. h) The mixture of $Pd(OAc)_2$ (0.1 mmol) and PPh_3 (0.4 mmol) was used as the catalyst. i) Purified yield through picrate formation.

Entries 20 and 21. The structure of **3** was determined by the comparison with the authentic sample, which was previously synthesized by the nickel-catalyzed homocoupling of 5-bromo-2-diethylaminotropone and the following hydrolysis.[9c] The dimerization of organic iodides is known to occur when the unreactive olefins such as trisubstituted compounds are used.[14] Therefore, it is remarkable that **1d** dimerizes in preference to vinylic substitution with the reactive styrene. The reactivity of halogen at the 3-position of the tropolone ring may be retarded sterically by the neighboring carbonyl or hydroxyl group, which prevents from the homocoupling of **1a**. The steric effect by the neighboring group was also examined by the reaction of 5-bromo-4-phenyltropolone **4** with styrene and methyl acrylate. The yields of the reaction products **5a** and **5b** (Entries 22 and 23) were considerably lower than those of **2j** and **2m** (Entries 10 and 17), in accordance with the reported results for sterically hindered halides.[14]

The reaction of 5-chlorotropolone **1e** with styrene did not occur even in a more prolonged reaction period (40 h). The difference in the reactivity of the halogen can be utilized for selective vinylation at a desired halogen position of polyhalotropolones. Divinylation of 3,7-dibromo-5-chlorotropolone **6** was carried out by the reaction with styrene to produce 5-chloro-3,7-distyryltropolone **7**. Such a selective dialkenylation at the iodinated carbons of polyhaloarenes in preference to the brominated carbons had reported recently.[16] It is noteworthy that 2-chlorotropone **8** reacted with styrenes to give 2-styryltropones **9a**—**9c**, though the yields were relatively low, probably by the steric factor found in the behavior of **1a**.

When both of the cis- and trans-isomers are produced in the vinylation products, the thermodynamically stable olefin is known to be favored.[14] The coupling constants of the vinylic protons (about 16 Hz) in the NMR spectra illustrate that most vinylated products are trans-isomers. However, some unresolved signals of aromatic and vinylic protons have been observed by superposition upon each other,



10a: $X^1=X^3=CO_2Et$, $X^2=NH_2$, $X^4=Br$
b: $X^1=X^3=H$, $X^2=NHAc$, $X^4=Br$
12: $X^1=Br$, $X^2=X^4=H$, $X^3=CO_2Et$
14a: $X^1=X^3=CO_2Et$, $X^2=Cl$, $X^4=H$
b: $X^1=X^3=X^4=H$, $X^2=I$

11a: $R^1=R^3=CO_2Et$, $R^2=NH_2$, $R^4=PhCH=CH$
b: $R^1=R^3=CO_2Et$, $R^2=NH_2$, $R^4=2\text{-}PyCH=CH$
c: $R^1=R^3=CO_2Et$, $R^2=NH_2$, $R^4=MeO_2CCH=CH$
d: $R^1=R^3=H$, $R^2=NHAc$, $R^4=PhCH=CH$
13a: $R^1=CO_2Et$, $R^2=R^4=H$, $R^3=PhCH=CH$
b: $R^1=CO_2Et$, $R^2=R^4=H$, $R^3=MeO_2CCH=CH$
15a: $R^1=R^3=CO_2Et$, $R^2=PhCH=CH$, $R^4=H$
b: $R^1=R^3=CO_2Et$, $R^2=2\text{-}PyCH=CH$, $R^4=H$
c: $R^1=R^3=CO_2Et$, $R^2=MeO_2CCH=CH$, $R^4=H$
d: $R^1=R^3=R^4=H$, $R^2=PhCH=CH$

Scheme 2.

and a further investigation should be done before determining which product is cis- or trans-isomer. Some kinds of palladium complexes are effective for the vinylation of **1c** with styrene (Entries 11 to 14). Tris(dibenzylideneacetone)dipalladium(0), $Pd_2(dba)_3\cdot CHCl_3$[17] was used as the reaction catalyst. Addition of triphenylphosphine to the system somewhat improved the yield, so that phosphine complexes appear to be favorable for the vinylic substitution. Divalent palladium complex $Pd_2Cl_4(PPh_3)_2$[18] as well as $Pd(OAc)_2$ can be used as the catalyst without interference of the tropolone moiety for chelation.

The vinylic substitution with olefins was then extended to azulene derivatives, using easily available 1-, 2-, and 6-haloazulenes[3d] as the starting materials. These results are listed in Table 2. Diethyl 2-amino-6-bromo-1,3-azulenedicarboxylate **10a** was made to react with styrene, 2-vinylpyridine, and methyl acrylate in a similar way to the vinylation of halotropolones to afford the corresponding 6-styryl- **11a**, 6-[2-(2-pyridyl)-vinyl]- **11b**, and 6-[2-(methoxycarbonyl)vinyl]azulene **11c** in fairly good yields. Similarly, 2-acetamido-6-bromoazulene **10b** gave 2-acetamido-6-styrylazulene **11d**. The bromine atom at the 1-position of **12** was easily replaced by the vinyl groups of styrene and methyl acrylate to give the corresponding vinylated azulenes **13a** and **13b**. It is remarkable that diethyl 2-chloro-1,3-azulenedicarboxylate **14a** reacted with all kinds of used olefins at the sterically crowded 2-position, and the corresponding 2-substituted azulenes **15a—15c** were obtained in moderate yields. Activation

Table 2. Vinylic Substitution of Haloazulenes (**10**, **12**, and **14**)[a]

Entry	Haloazulene	Olefin	Product	Yield (%)[b]
1	**10a**	Styrene	**11a**	(70)
2	**10a**	2-Vinylpyridine	**11b**	(89)
3	**10a**	Methyl acrylate	**11c**	(99)
4	**10b**	Styrene	**11d**	(85)
5	**12**	Styrene	**13a**	(66)
6	**12**	Methyl acrylate	**13b**	(88)
7	**14a**	Styrene	**15a**	(21)
8	**14a**	2-Vinylpyridine	**15b**	(52)
9	**14a**	Methyl acrylate	**15c**	(57)
10	**14b**	Styrene	**15d**	(30)

a) The reactions were carried out in the same manner as in Table 1. b) Isolated yields based on haloazulenes after purification by column chromatography.

of the chlorine atom at the 2-position may be attributed to the electron-withdrawing character of the neighboring ethoxycarbonyl groups. A similar phenomenon was reported in the reaction of **14a** with copper(I) phenylacetylide.[13] As for the synthesis of unsubstituted azulenes except for the unsaturated carbon chain in question, the reaction of 2-iodoazulene **14b** with styrene was carried out to give 2-styrylazulene **15d**, which had previously been synthesized by partial hydrogenation of the corresponding ethynyl compound[13] or by condensation of 2-methylazulene with benzaldehyde.[19] The results mentioned above show that the vinylation reaction catalyzed by palladium complexes can be effectively applied to most of azulenes, tropolones, and related compounds, and that the reaction will be a handy tool for preparing a conjugated carbon chain at the desired halogen position on the nonbenzenoid aromatic compounds.

Experimental

Melting points were obtained by a Yanaco Micro-melting point apparatus and are uncorrected. The IR spectra were recorded on a Hitachi 215 using KBr disk. Most of the ^{1}H NMR spectra were measured on a Hitachi R-22 spectrometer (90 MHz) using TMS as the internal standard, and some spectra were obtained by a Hitachi 90H FT-NMR spectrometer (90 MHz). The UV-visible spectra were recorded on a Hitachi 340 spectrophotometer. Elemental analyses were performed by the Instrumental Analysis Center for Chemistry, Faculty of Science, Tohoku University. Solvents used for the reactions were distilled over sodium, and stored under an inert atmosphere. Chromatography was done on a 300 mesh silica gel (Wako C-300). Palladium complexes, $Pd(PPh_3)_4$,[20] and $Pd_2(dba)_3 \cdot CHCl_3$ (dba=dibenzylideneacetone),[17] were prepared according to the literatures. The following haloazulenes and halotropolones were also prepared according to the literatures: 3-iodotropolones **1a**,[21] 4-bromotropolone **1b**,[22] 5-bromo- **1c**,[23] 5-chloro- **1e**,[23] and 5-iodotropolone **1d**,[23] 2-chlorotropone **8**,[24] diethyl 2-amino-6-bromo-1,3-azulenedicarboxylate **9a**,[25] 2-acetamido-6-bromoazulene **9b**,[26] ethyl 3-bromo-1-azulenecarboxylate **12**,[27] diethyl 2-chloro-1,3-azulenedicarboxylate **14a**,[25] and 2-iodoazulene **14b**.[25]

As the typical procedures, the reactions of **1a**, **1d**, **8**, and **10a** with styrene are given as follows.

3-Styryltropolone 2a: The ampoule (60 cm^3) was purged with nitrogen, and **1a** (545 mg, 2 mmol) and $Pd(PPh_3)_4$ (120 mg, 0.1 mmol) were placed successively. The mixture was dissolved in deaerated THF (10 cm^3), and styrene (0.7 cm^3, 6.1 mmol) and triethylamine (0.7 cm^3) were added as rapidly as possible. The ampoule was sealed, and heated in an oil bath at 100—110 °C for 20 h. The reaction mixture was transferred into a flask equipped with a rotatory evaporator, and concentrated under reduced pressure. The residue was dissolved in benzene (30 cm^3), and extracted with 5% NaOH solution (50 cm^3×3). Acidification of the solution with 6 M HCl (M=mol dm^{-3}) gave a white turbid solution, which was then extracted with ethyl acetate. After the solution was dried (Na_2SO_4) and concentrated under reduced pressure, the yellow oil (298 mg) obtained was chromatographed on silica gel (9.0 g) using benzene as an eluent, to give yellow crystals of **2a** (173 mg, 39%), mp 58—62 °C. Recrystallization from ethanol raised the melting point of **2a** up to 73—75 °C. (lit,[28] mp 111.5—112.5 °C; Discrepancy between the melting points of **2a** and the authentic sample is unexplainable yet, but the following spectra of **2a** are consistent with the strucure of 3-styryltropolone). IR (KBr) 3160 (OH), 1650, 1550 (CO, C=C), 685 (Ph) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=6.95—7.65 (10H, m), 7.83 (1H, d, J=6 Hz). Found: C, 80.23; H, 5.63%. Calcd for $C_{15}H_{12}O_2$: C, 80.33; H, 5.39%.

3-[2-(*p*-Methoxyphenyl)vinyl]tropolone 2b: Mp 134—136 °C (benzene); IR (KBr) 3170 (OH), 1605, 1580 (C=C, CO), 1250 (C–O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.78 (3H, s), 6.82 (1H, d, J=12 Hz), 7.29 (2H, d, J=11 Hz), 7.32 (2H, d, J=12 Hz), 6.90—7.65 (8H, m), 7.77 (1H, d, J=10 Hz). Found: C, 75.73; H, 5.44%. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55%.

3-[2-(2-Pyridyl)vinyl]tropolone 2c: Mp 96—97.5 °C (benzene–cyclohexane); IR (KBr) 3230 (OH), 1585, 1530 (CO, C=N) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=6.95—8.25 (10H, m), 8.58 (1H, d, J=6 Hz). Found: C, 74.93; H, 4.84; N, 6.16%. Calcd for $C_{14}H_{11}O_2N$: C, 74.65; H, 4.92; N, 6.22%.

3-(2-Carboxyvinyl)tropolone 2d: Mp 224 °C (decomp) (EtOH) (lit,[29] mp 233—235 °C). IR (KBr) 3180—2300, 1685 (carboxyl), 1620, 1600 (CO, C=C) cm^{-1}.

3-(3-Carboxy-1-propenyl)tropolone 2e: Mp 155 °C (EtOH); IR (KBr) 3180 (OH), 3100—2550 (carboxyl), 1720—1690 (CO) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.73 (2H, d, J=7 Hz), 6.48 (1H, d, J=16 Hz), 6.9—7.3 (4H, m), 7.69 (1H, d, J=11 Hz). Found: C, 63.89; H, 4.88%. Calcd for $C_{11}H_{10}O_4$: C, 64.07; H, 4.89%.

3-(3-Cyano-1-propenyl)tropolone 2f: Mp 74—75 °C (benzene–hexane); ^{1}H NMR ($CDCl_3$) δ=3.48 (2H, d, J=6 Hz), 6.48 (1H, d, J=16 Hz), 6.9—7.5 (4H, m), 7.61 (1H, d, J=11 Hz). Found: C, 70.53; H, 4.86; N, 7.42%. Calcd for $C_{11}H_9O_2N$: C, 70.58; H, 4.85; N, 7.48%.

3-[3-(3,4-Dimethoxyphenyl)-1-propenyl]tropolone 2g: Mp 80—81 °C (benzene–EtOH); IR (KBr) 3200 (OH), 1605, 1550 (C=C, C=O), 1240 (C–O) cm^{-1}; ^{1}H NMR (CCl_4) δ=3.61 (2H, d, J=6 Hz), 3.72 (3H, s), 3.75 (3H, s), 6.30 (1H, d, J=14 Hz), 6.53—6.95 (5H, m), 7.14—7.15 (2H, m), 7.45 (1H, d, J=11 Hz). Found: C, 72.40; H, 6.13%. Calcd for $C_{18}H_{18}O_4$: C, 72.46; H, 6.08%.

3-[3-(3,4-Methylenedioxyphenyl)-1-propenyl]tropolone 2h: Mp 106—107.5 °C (EtOH); IR (KBr) 3170 (OH), 1620, 1560 (CO, C=C), 1260 (C–O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.69 (2H, d, J=6 Hz), 5.85 (2H, s), 6.10—6.30 (2H, m), 6.50—7.30 (6H, m), 7.45 (1H, d, J=11 Hz). Found: C, 72.23; H, 4.97%. Calcd for $C_{17}H_{14}O_2$: C, 72.33; H, 5.00%.

4-Styryltropolone 2i: Mp 85—87 °C (lit,[30] mp 90—91 °C). IR (KBr) 3200 (OH), 1590, 1530, (CO, C=C), 690 (Ph) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=6.63 (1H, d, J=11 Hz), 6.85—7.65 (10H, m).

5-Styryltropolone 2j: Mp 133—135 °C (lit,[31] mp 131—132 °C); IR (KBr) 3220 (OH), 1615, 1530 (CO, C=C), 690 (Ph) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=7.25—7.52 (9H, m), 7.60 (2H, d, J=7 Hz).

5-[2-(*p*-Methoxyphenyl)vinyl]tropolone 2k: Mp 194—195 °C (EtOH) (lit,[31] mp 195 °C); IR (KBr) 3150 (OH), 1610, 1550 (CO, C=C), 1275, 1255, 1180 (C–O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=3.82 (3H, s), 6.95 (3H, m), 7.25—7.65 (7H, m).

5-[2-(2-Pyridyl)vinyl]tropolone 2l: Mp 140.5—141.5 °C

(EtOH); IR (KBr) 3240, (OH), 1620, 1590, 1555 (C=C, CO, C=N) cm^{-1}; ^1H NMR ($CDCl_3$) δ=6.95—7.80 (10H, m), 8.59 (1H, d, J=7 Hz). Found: C, 74.46; H, 4.85; N, 6.13%. Calcd for $C_{14}H_{11}O_2N$: C, 74.65; H, 4.92; N, 6.22%.

5-(2-Carboxyvinyl)tropolone 2m: Mp 238—239 °C (decomp) (EtOH) [lit,[29] mp 239 °C (decomp)]; IR (KBr) 3200—2500, 1700 (carboxyl), 1615, 1565 (CO, C=C) cm^{-1}; ^1H NMR (DMSO-d_6) δ=6.42 (1H, d, J=16 Hz), 7.12 (2H, d, J=11 Hz), 7.50 (2H, d, J=16 Hz), 7.70 (2H, d, J=11 Hz).

5-[3-(3,4-Dimethoxyphenyl)-1-propenyl]tropolone 2n: Mp 140.5—142 °C (EtOH); IR (KBr) 3200 (OH), 1610, 1550 (C=C, C=O), 1270, 1215, 1140 (C-O) cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.50 (2H, d, J=7 Hz), 3.88 (6H, s), 6.32 (1H, m), 6.75—6.95 (3H, m), 7.30 (5H, s), 7.32 (1H, s). Found: C, 72.21; H, 6.17%. Calcd for $C_{18}H_{18}O_4$: C, 72.46; H, 6.08%.

5-[3-(3,4-Methylenedioxyphenyl)-1-propenyl]tropolone 2o: Mp 123—124 °C (EtOH); IR (KBr) 3230 (OH), 1620, 1550 (C=C, CO), 1260, 1210 (C-O) cm^{-1}; ^1H NMR ($CDCl_3$) δ=3.52 (2H, d, J=7 Hz), 5.92 (2H, s), 6.32 (1H, m), 6.78 (3H, m), 7.30 (4H, s), 7.96 (1H, s). Found: C, 72.38; H, 5.03%. Calcd for $C_{17}H_{14}O_4$: C, 72.33; H, 5.00%.

Formation of 5,5′-Bitropolone 3: A mixture of **1d** (545 mg, 2.0 mmol), styrene (0.6 cm^3), $Pd(PPh_3)_4$ (120 mg, 0.1 mmol), triethylamine (0.8 cm^3) in THF (10 cm^3) was heated at 115—120 °C for 21 h, and the resulting mixture was treated similarly. Acidification of the alkaline solution with 6 M HCl yielded brownish yellow precipitates, which were collected by filtration, and washed with ethyl acetate (50 cm^3) to give 106 mg (0.44 mmol, 44%) of **3**; mp 255 °C (decomp), which was identical with the authentic sample[9c] by the comparison of their IR spectra [lit,[9c] 260 °C (decomp)]; IR (KBr) 3460 (OH), 1620, 1552 (C=C, CO) cm^{-1}; ^1H NMR (DMSO-d_6) δ=7.52 (4H, d, J=12 Hz), 7.84 (4H, d, J=12 Hz). The filtrate was extracted with ethyl acetate, which was combined with the solvent used for washing the precipitates, and dried over Na_2SO_4. Concentrating the solution followed by extracting the residue with ethanol gave 38 mg (0.17 mmol, 8.5%) of **2j**.

5-Bromo-4-phenyltropolone 4: To a solution of 5-amino-4-phenyltropolone[32] (1.28 g, 6.0 mmol) in dioxane (10 cm^3) and water (6 cm^3), concd H_2SO_4 (1.0 cm^3) and then a solution of sodium nitrite (0.50 g, 7.2 mmol) in water (2 cm^3) were added at 0—5 °C in 15 min. After the successive addition of copper(I) bromide (2.20 g, 15.3 mmol) and 48% HBr (8 cm^3) during 15 min, the solution was stirred for 1 h, until the temperature reached to room temperature. Then the solution was heated at 60 °C for 10 min, and poured into water (60 cm^3). The produced precipitates (1.60 g) were dissolved in dichloromethane (100 cm^3), and treated with a flow of hydrogen sulfide. After evaporating the solvent, crystallization from ethanol gave yellow crystals of **3** (1.25 g, 75%). Mp 188—189 °C ($CHCl_3$–EtOH); IR (KBr) 3230 (OH), 1600, 1550 (C=C, C=O) 700 (Ph) cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.07 (1H, d, J=12 Hz), 7.21 (1H, s), 7.22—7.43 (5H, m), 7.80 (1H, d, J=12 Hz). Found: C, 56.58; H, 3.45%. Calcd for $C_{13}H_9O_2Br$: C, 56.34; H, 3.27%.

4-Phenyl-5-styryltropolone 5a: Mp 95—96 °C (EtOH); IR (KBr) 3200 (OH), 1600, 1530 (C=C, C=O), 700 (Ph) cm^{-1}; ^1H NMR ($CDCl_3$) δ=6.86 (1H, d, J=11 Hz), 7.0—7.7 (13H, m), 7.88 (1H, d, J=11 Hz). Found: C, 79.00; H, 5.13%. Calcd for $C_{21}H_{16}O_2$: C, 79.02; H, 5.00%.

5-(2-Carboxyvinyl)-4-phenyltropolone 5b: Mp 242—243 °C (THF); IR (KBr) 3150 (OH), 3050—2550 (carboxyl), 1590, 1560 (C=C, C=O), 695 (Ph) cm^{-1}; ^1H NMR (THF-d_8) δ=6.25 (1H, d, J=16 Hz), 7.10—7.45 (7H, m), 7.20 (1H, d, J=16 Hz), 7.85 (1H, d, J=11 Hz). Found: C, 71.18; H, 4.68%. Calcd for $C_{16}H_{12}O_4$: C, 71.68; H, 4.51%.

5-Chloro-3,7-distyryltropolone 7: Mp 185 °C ($CHCl_3$–EtOH); IR (KBr) 3050 (OH), 1625, 1550 (C=C, C=O), 690 (Ph) cm^{-1}; ^1H NMR ($CDCl_3$) δ=7.15—7.20 (1H, t, J=5 Hz), 7.20—7.40 (7H, m), 7.45—7.60 (6H, m), 7.70—7.90 (3H, m). Found: C, 76.28; H, 4.87%. Calcd for $C_{23}H_{17}O_2Cl$: C, 76.55; H, 4.75%.

2-Styryltropone 9a: A mixture of **8** (280 mg, 2.0 mmol), styrene (310 mg, 3.0 mmol), and triethylamine (0.4 cm^3) in THF (15 cm^3) was heated at 120 °C for 18 h in the presence of $Pd(PPh_3)_4$ (120 mg, 0.1 mmol) in a sealed tube. After filtration of palladium that had been deposited during the reaction, the filtrate was concentrated, and the residue was chromatographed on silica gel (10 g) using benzene–ethyl acetate (1:0—1:1). Evaporation of the benzene–ethyl acetate (10:1) eluent gave yellow crystals of **9a** (102 mg, 49.0%), which were recrystallized from carbon tetrachloride: Mp 91—92 °C (CCl_4) (lit,[33] mp 94—95 °C); IR (KBr) 1620, 1565 (C=C, C=O) cm^{-1}; ^1H NMR ($CDCl_3$) δ=6.85—7.10 (4H, m), 7.20—7.65 (8H, m).

2-[2-(*p*-Methoxyphenyl)vinyl]tropone 9b: Mp 93—95 °C (benzene) (lit,[33] mp 98 °C); IR (neat) 1625, 1580 (C=C, C=O) cm^{-1}. (Found: C, 79.57; H, 5.94%).

2-[2-(2-Pyridyl)vinyl]tropone 9c: Mp 90—91.5 °C (benzene–cyclohexane); picrate, mp 202—204 °C (decomp); IR (KBr) 1625, 1570 (C=C, CO, C=N), 770 cm^{-1}; ^1H NMR ($CDCl_3$) δ=6.75—7.10 (4H, m), 7.30—7.70 (6H, m). Found: C, 80.27; H, 5.22; N, 6.62%. Calcd for $C_{14}H_{11}ON$: C, 80.36; H, 5.30; N, 6.69%.

Diethyl 2-Amino-6-styryl-1,3-azulenedicarboxylate 11a: A THF solution (10 cm^3) of **10a** (735 mg, 2 mmol), $Pd(PPh_3)_4$ (120 mg, 0.1 mmol), styrene (1.2 cm^3, 10.5 mmol), and triethylamine (1.5 cm^3) was sealed in an ampoule (60 cm^3). After heating in an oil bath at 110—120 °C for 18 h, the mixture was concentrated under reduced pressure, and then the residue was chromatographed on silica gel (10 g). Elution with a mixture of benzene and ethyl acetate (1:1) gave reddish-orange crystals of **11a** (551 mg, 70%). Mp 148—149 °C (EtOH) (lit,[34] mp 147.5—148 °C); IR (KBr) 3450, 3350 (NH_2), 1680 (ester), 990 (Ph) cm^{-1}. (Found: C, 74.32; H, 5.92; N, 3.54%).

Diethyl 2-Amino-6-[2-(2-pyridyl)vinyl]-1,3-azulenedicarboxylate 11b: Mp 146—148 °C (benzene); IR (KBr) 3480, 3340 (NH_2), 1680 (ester) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.47 (6H, t, J=7 Hz), 4.46 (4H, q, J=7 Hz), 7.04—7.35 (4H, m), 7.55—7.82 (5H, m), 8.54 (1H, d, J=5 Hz), 8.98 (2H, d, J=11 Hz); UV (MeOH) 250 (log ε 4.53), 349 (4.75), 454 nm (4.49). Found: C, 71.04; H, 5.38; N, 6.92%. Calcd for $C_{23}H_{22}O_4N_2$: C, 70.75; H, 5.18; N, 7.18%.

Diethyl 2-Amino-6-[2-(methoxycarbonyl)vinyl]-1,3-azulenedicarboxylate 11c: Mp 197—198 °C (THF); IR (KBr) 3490, 3350 (NH_2), 1705, 1685, 1650 (ester) cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.50 (6H, t, J=7 Hz), 3.80 (3H, s), 4.46 (4H, q, J=7 Hz), 6.47 (1H, d, J=16 Hz), 7.50—7.90 (5H, m), 9.01 (2H, d, J=11 Hz); UV (EtOH) 248 (log ε 4.29), 340 (4.61), 447 nm (4.19). Found: C, 64.66; H, 5.74; N, 3.71%. Calcd for $C_{20}H_{21}O_6N$: C, 64.68; H, 5.70; N, 3.77%.

2-Acetamido-6-styrylazulene 11d: Mp 257 °C (THF); IR (KBr) 3290 (NH), 1600, 1595, 1570, 1530 (amide) cm^{-1};

^{1}H NMR (DMSO-d_6) δ=3.10 (3H, s), 7.10—7.70 (11H, m), 8.35 (2H, d, J=16 Hz), 11.50 (1H, s); UV (MeOH) 224 (log ε 4.50), 313 (4.70), 325 (4.70), 411 (4.58), 432 (4.59), 559 nm (2.72). Found: C, 78.14; H, 6.00; N, 4.45%. Calcd for $C_{20}H_{17}ON \cdot H_2O$: C, 78.66; H, 6.27; N, 4.59%.

Ethyl 3-Styryl-1-azulenecarboxylate 13a: Mp 80—82 °C (EtOH); IR (KBr) 1690 (ester), 1215—1205 (C-O), 690 (Ph) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.49 (3H, t, J=7 Hz), 4.47 (2H, q, J=7 Hz), 7.10—7.70 (10H, m), 8.54 (1H, d, J=9 Hz), 8.67 (1H, s), 9.48 (1H, d, J=9 Hz); UV (MeOH) 237 (log ε 4.22), 277 (4.28), 316 (4.60), 395 (4.44), 409 (3.94), 597 nm (2.70). Found: C, 83.52; H, 6.02%. Calcd for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00%.

Ethyl 3-[2-(Methoxycarbonyl)vinyl]-1-azulenecarboxylate 13b: Mp 114—115.5 °C (benzene); IR (KBr) 1690, 1620 (ester), 1220, 1160 (C-O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.45 (3H, t, J=7 Hz), 3.80 (3H, s), 4.45 (2H, q, J=7 Hz), 6.45 (1H, d, J=16 Hz), 7.40—7.85 (3H, m), 8.20 (1H, d, J=16 Hz), 8.85—8.70 (2H, m), 9.58 (1H, d, J=11 Hz); UV (MeOH) 247 (log ε 4.37), 306 (4.65), 346 (sh, 4.31), 387 (4.19), 551 nm (2.95). Found: C, 71.59; H, 5.63%. Calcd for $C_{17}H_{16}O_4$: C, 71.82; H, 5.67%.

Diethyl 2-Styryl-1,3-azulenedicarboxylate 15a: Mp 79—81 °C (EtOH); IR (KBr) 1670 (ester), 1200, 1170 (C-O), 990 (Ph) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.23 (6H, t, J=7 Hz), 4.44 (2H, q, J=7 Hz), 6.82 (1H, d, J=16 Hz), 7.22—7.80 (10H, m), 8.04 (1H, d, J=16 Hz); UV (MeOH) 230 (log ε 4.24), 292 (4.34), 335 (4.48), 397 (3.89), 527 nm (2.54).

Diethyl 2-[2-(2-Pyridyl)vinyl]-1,3-azulenedicarboxylate 15b: Mp 95—97.5 °C (EtOH); IR (KBr) 1670 (ester), 1200, 1175 (C-O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.37 (6H, t, J=7 Hz), 4.47 (4H, q, J=7 Hz), 6.92 (1H, d, J=17 Hz), 7.05—7.85 (7H, m), 8.48 (1H, d, J=17 Hz), 9.35 (2H, d, J=12 Hz); UV (MeOH) 230 (log ε 4.33), 330 (4.67), 392 (sh, 4.00), 530 nm (3.19). Found: C, 73.83; H, 5.71; N, 3.62%. Calcd for $C_{23}H_{21}O_4N$: C, 73.58; H, 5.64; N, 3.73%.

Diethyl 2-[2-(Methoxycarbonyl)vinyl]-1,3-azulenedicarboxylate 15c: Mp 93—94 °C; IR (KBr) 1720, 1685 (ester), 1190, 1180 (C-O) cm^{-1}; ^{1}H NMR ($CDCl_3$) δ=1.88 (6H, t, J=7 Hz), 3.80 (3H, s), 4.40 (4H, q, J=7 Hz), 6.06 (1H, d, J=18 Hz), 7.68 (2H, d, J=11 Hz), 7.79 (1H, t, J=11 Hz), 8.47 (1H, d, J=18 Hz), 9.40 (2H, d, J=11 Hz); UV (MeOH) 236 (log ε 4.34), 306 (4.72), 355 (3.91), 529 nm (2.78). Found: C, 67.18; H, 5.77%. Calcd for $C_{20}H_{20}O_6$: C, 67.40; H, 5.66%.

2-Styrylazulene 15d: Mp 207—208 °C (benzene) (lit,[19] mp 207—208 °C). The IR spectrum of **15d** was identical with the authentic sample.[19]

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