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Thermal Rearrangement of 2,5-Bis(allyloxy)tropone, Revisited. Formation of Four Thermolysates under the Claisen Rearrangement Conditions and Structure Revision of the Major Thermolysate

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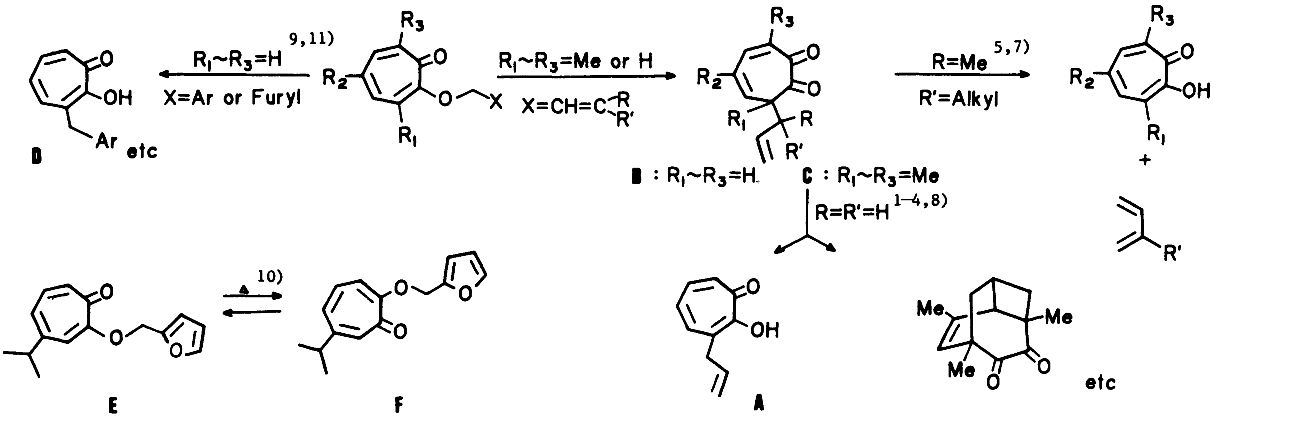
A reinvestigation of the Claisen rearrangement of 2,5-bis(allyloxy)tropone led to the isolation of three diallyl-5-hydroxytropolones along with an intermediary thermolysate, 3-allyl-5-allyloxytropolone. The structure of the formerly identified product was revised from 3,6-diallyl-5-hydroxytropolone to 4,6-diallyl-5-hydroxytropolone. The involvement of no cleavage-recombination process was established by cross-over deuterium labelling experiments. These derivatives were respectively converted to *p*-tropoquinones, one of which was further converted to a cyclohepta[*b*]pyranone derivative by an electrochemical reaction.

The Claisen-type [3,3] sigmatropy of a troponoid derivatives has revealed anomalous features; unsubstituted allyl and propargyl ethers of tropolones gave rearrangement products (**A**) in excellent yields.[1–4] However, allyl groups having a hydrogen-carrying substituent at C-3, e.g., 3-methyl-2-butenyl (prenyl) ethers of tropolones, gave rearrangement products in low yields[2,5] due to a consecutive occurrence of a Woodward–Hoffmann rule-allowed[6] [$_\pi 6+_\sigma 2+_\sigma 2$] process from the proto-Claisen products (**B**).[7] The intramolecular Diels–Alder reaction of Claisen products from 2-allyloxy- and 2-propynyloxy-3,5,7-trimethyltropones constitutes a trapping of unaromatizable protoproducts (**C**).[8] The arylmethoxy- and heteroarylmethoxytropones, which are superficially capable of concerted sigmatropic reactions, yielded homolytic rearrangement products, 3- or/and 5-arylmethyl- and heteroarylmethyltropolones (**D**).[9–11] A sort of degenerated [1,9] sigmatropy[12] was conceived to occur prior to the rearrangement; the heating of two isomeric 2-furylmethyl ethers (**E** and **F**) prepared from hinokitiol (4-isopropyltropolone) gave thermolysates in the same yields.[10] Furthermore, thermolysis in dimethylsulfoxide caused an oxidative fragmentation to carbonyl compounds.[13] These chemical properties of tropolonyl ethers made their thermal reactions very complicated.

A decade ago, we investigated the Claisen rearrangement of 2,5-bis(allyloxy)tropone (**1**) and its various derivatives in order to construct several heterocyclic troponoids, e.g., cycloheptadifurans.[14] From parent **1**, we isolated yellow crystalline thermolysate (**2**) in 39% yield, and assigned it to 3,6-diallyl-5-hydroxytropolone from a mechanistic view point. Although the ^{1}H NMR spectrum of **2** or its acetate (**3**) revealed overlapped signals, indicating the presence of a symmetry element in the molecule, we simply thought that this phenomenon was accidental. During our recent studies regarding the preparation of various *p*-tropoquinone derivatives[15] and their cyclic voltammetry (CV) analysis,[16,17] we have reinvestigated the Claisen rearrangement of **1**, and have found the occurrence of four rearrangement products, suggesting the complicated pathways involved.



Scheme 1.

In this paper, we describe the structural determination of these thermolysates; this eventually leads to a revision of the structure of former thermolysate, **2**, from 3,6-diallyl-5-hydroxytropolone to 4,6-diallyl-5-hydroxytropolone, and the deuterium-labelling experiments to prove the intramolecular nature of this rearrangement.

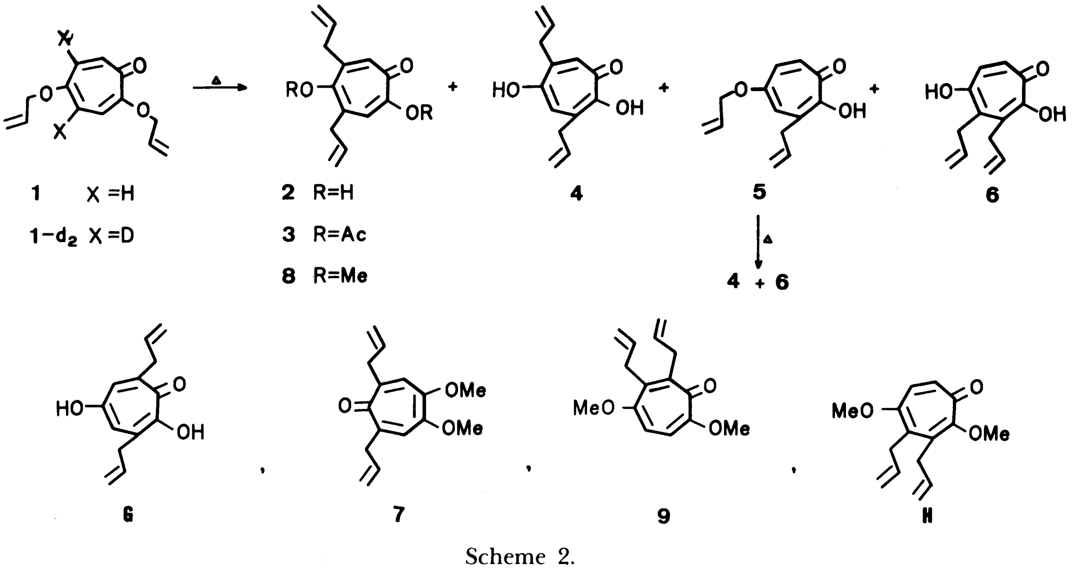
Results and Discussion

When **1** was refluxed in xylene for 2 h,14) four products (**2**, **4**, **5**, and **6**) were formed; however, only three of them (**2**, **4**, and **5**) were detectable on the thin-layer chromatogram (TLC). The major products (**2** and **5**) were isolated by a silica-gel column chromatography and were identical with the previous samples.14) Repeated silica-gel column chromatography of the intermediary fractions gave another product, **4**. Its ^{13}C and ^{1}H NMR spectra revealed no element of symmetry and no spin–spin coupling between the protons on the seven-membered ring. Consequently, it must be 3,6-diallyl-5-hydroxytropolone; thus, the previously assigned structure of **2** should be revised. These facts suggest that the structure of **2** is either 3,7-diallyl-5-hydroxytropolone (**G**) or 4,6-diallyl-5-hydroxytropolone. To differentiate the point, **2** was converted to two methyl ethers (**7** and **8**) by a treatment with diazomethane. The mixture could be fractionated by silica-gel column chromatography; the ^{1}H NMR spectrum of **8** revealed two aromatic proton signals at different fields (δ=6.59 and 7.15); however, that of **7** showed an overlapped signal for two protons at 7.32. In parallel, the ^{13}C NMR spectrum of **7** showed only eight signals but that of **8** showed fifteen well-resolved lines. If **2** were **G**, **8** should be formulated as 3,7-diallyl-2,5-dimethoxytropone, and its ^{1}H NMR spectrum must exhibit mutually spin-coupled C-4 and C-6 protons (as in the cases of **1**, **10**, and **5**) whose spin–spin coupling constants fall in a range of ca. J=3 Hz.14) As mentioned, the aromatic proton signals of **8** appeared as two singlet lines. Moreover, the chemical shift of the aromatic protons of **7**, at 7.32, closely resembled the C-3 proton of 4,5-dimethoxytropone. Therefore, **2** must be 4,6-diallyl-5-hydroxytropolone.

From the later fractions of chromatography the third methyl ether (**9**) was isolated, which should be derived from the remaining thermolysate, **6**. Although the isolation of **6** from the thermolysis mixture failed, it was independently prepared in 12% yield together with **4**, in 72% yield, by a further thermolysis of **5**. The samples of methyl ether, **9**, prepared from both sources were mutually identical. The ^{1}H NMR of **6** revealed a pair of AB-signals (J=12 Hz) ascribable to vicinal protons on the seven-membered ring, indicating **6** to be 3,4-diallyl-5-hydroxytropolone and, hence, **9**, 2,3-diallyl-4,7-dimethoxytropone. The undetectability of the isomer, 3,4-diallyl-2,5-dimethoxytropone (**H**) in the methylation product of **6** must be explained in terms of a steric effect.

The product, **5**, was 3-allyl-5-allyloxytropolone. Among the thermolysates, **4** was the expected Claisen rearrangement product, while the major product, **2**, was an abnormal thermolysate, whose formation should involve complicated rearrangement processes.

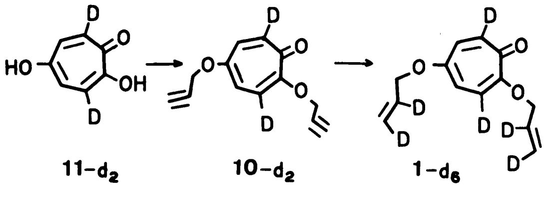
In order to elucidate the mechanism, we analyzed the isotope distributions of the thermolysates of the deuterio derivatives of **1**, 2,5-bis(allyloxy)tropone-4,6-d_2 (**1**-d_2) and 2,5-bis(allyl-2,3-d_2-oxy)tropone-3,7-d_2 (**1**-d_6). The **1**-d_2 was prepared by a condensation of 3-bromo-1-propene with 5-hydroxytropolone-4,6-d_2 (**11**-4,6-d_2).18) The **1**-d_6 was prepared by catalytic deuteration with Lindlar's catalyst of 2,5-bis(2-propynyloxy)tropone-3,7-d_2 (**10**-d_2), prepared by a condensation of 5-hydroxytropolone-3,7-d_2 (**11**-3,7-d_2) with 3-bromo-1-propyne.



Scheme 2.

The thermolysis of **1**-d_2 determined the location of the allyl groups; the major thermolysate, **2**-*d*, caused a loss of two deuterium atoms, while **4**-*d* retained half of the deuterium atoms and **5**-*d* lost only a fractional amount of deuterium atoms. Table 1 shows a mass-spectral analysis of these thermolysates.

When a 1:2-mixture of **1**-d_6 and **1**-d_0 was heated under similar conditions, again the mass spectrometry of the products isolated after silica-gel column chromatography eliminated the radical dissociation-recombination mechanism; the major product, **2**-*d*, revealed identical deuterium distributions with that of the starting material within the experimental error; i.e., its mass spectrometry deduced to be **2**-d_6 and **2**-d_0 (1:2), and there was no **2**-d_2 or **2**-d_4. Therefore, **2** had been formed by the intramolecular process throughout. Table 2 demonstrates the deuterium distributions of **2**-*d* and other thermolysates to confirm the conclusion. In the cases of **4**-*d* and **5**-*d*, an approximate 1:2:1-distribution of d_4-, d_5-, and d_6-components did not contradict the suggested mechanism, since there were substantial amounts of **1**-d_7 in the starting material. Probably, a partial deuterium exchange of the acidic hydrogen on the sp-carbon might have taken place prior to catalytic deuteration.



Scheme 3.

Table 1. The Mass-Spectral Determinations of Deuterium Contents of Thermolysates from **1**-d_2

Compound	*m*/*z* 218(d_0)	219(d_1)	220(d_2)	221(d_3)	222(d_4)
1-d_2	3.2	4.4	53.2	23.2	16.0
2-*d*	55.7	17.6	18.5	8.3	
4-*d*	27.6	50.4	20.7	1.4	
5-*d*	2.0	10.5	49.8	34.5	3.2

Interestingly, the thermolysis of **5** gave only **4** and **6**, whose formation must be straightforward. Hence, **2** might be derived from an undetected intermediary protoproduct (**J**). If it occurred via thermally-allowed concerted processes, either a), two-fold [3,3] sigmatropies, or b), consecutive [3,7] and [3,3] sigmatropies, should be considered, but the deuterium distributions can not distinguish these two routes. In this particular system, the [3,7] process, however, requires a relatively long-distance flight of the allyl group from C-2 oxygen to the C-5 oxygen; in such a case, the [3,7] process should be the rate-determining step of the rearrangement. The absence of the intermediate thermolysates from **J** to **2** may suggest that the possibility is unfavorable.[19]

In addition, the DDQ (2,3-dichloro-5,6-dicyano-*p*-benzoquinone)-oxidation of **4**, similar to that of **2**,[15] afforded 3,6-diallyl-*p*-tropoquinone (**12**) in good yield. The NMR spectra were consistent to the structure assigned in the present study.

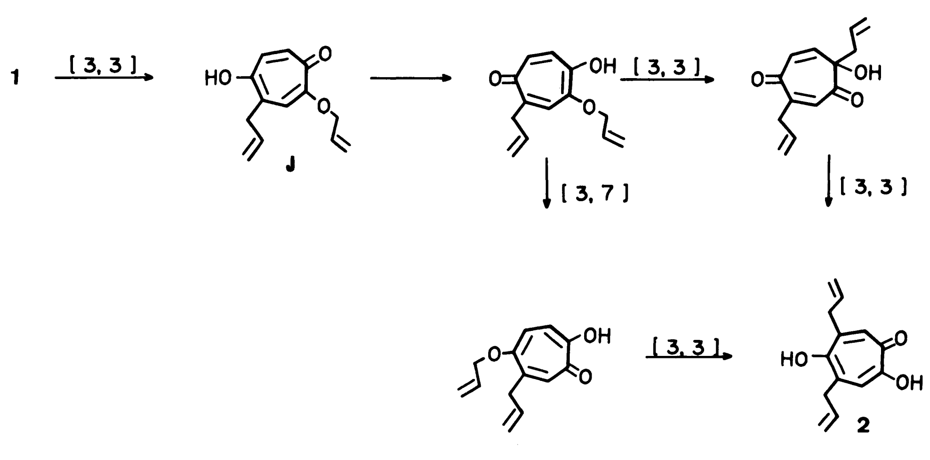
Finally, we wish to record the results of an electrolytic reduction of **13**, 4,6-diallyl-*p*-tropoquinone, obtained from the major thermolysate, **2**. As described in the preliminary paper, the CV of several *p*-tropoquinones exhibited an extra oxidation wave after returned at the second oxidation wave.[20] For this extra wave, we assumed the occurrence of a side reaction from the quinones. When **13**, of which the wave was indeed the most pronounced one, was electrolyzed in an *N*,*N*-dimethylformamide (DMF) solution in the presence of a supporting electrolyte, tetrabutylammonium tetrafluoroborate (TBAT) at −0.4 V for 25 h,[21] the formation of a product (**14**) was detected by a TLC analysis. The NMR evidence showed the structure of **14** to be 9-allyl-7-hydroxycyclohepta[*b*]pyran-6(2*H*)-one; particularly, a related model compound, 2-methylfuro[3′,2′:3,4]cyclohepta[1,2-*b*]pyran-4(8*H*)-one (**K**), identified previously among the Claisen rearrangement products of **10**, provided a closely resembled ^{1}H NMR spectral feature.[14]

Consequently, at least in the case of **13**, the irreversible extra oxidation wave was explainable in terms of the chemical reaction. However, the wave has appeared in the alkyl-*p*-tropoquinones, which should

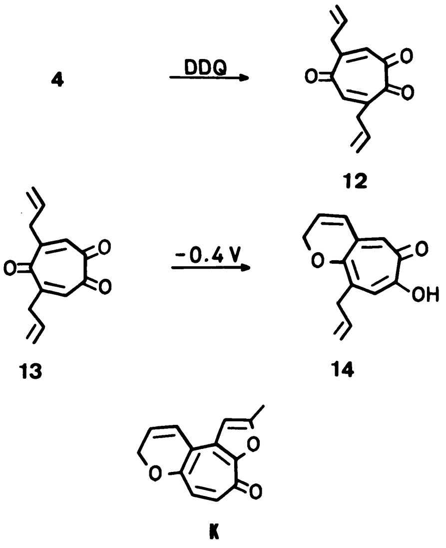
Table 2. The Deuterium Distributions of the Starting Material and the Thermolysates Obtained from a 1:2-Mixture of **1**-d_6 and **1**-d_0

Compound	*m*/*z* 218(d_0)	219(d_1)	220(d_2)	221(d_3)	222(d_4)	223(d_5)	224(d_6)	225(d_7)
1-d_6	14.8	4.6	2.1	4.2	8.3	23.1	25.8	17.6[a]
1-(d_6+d_0)	71.1	2.6	1.3	1.4	2.9	8.4	9.6	2.6
2-*d*	68.2	1.9	0.3	1.2	3.9	8.9	13.7	2.0
4-*d*	64.6	2.0	3.4	3.1	7.9	11.7	5.5	1.8
5-*d*	70.6	1.9	1.2	1.8	6.8	12.8	4.0	0.8

a) These figures show that the sample of **1**-d_6 contains nearly equal amount of **1**-d_5, together with some amounts of **1**-d_7.



Scheme 4.



Scheme 5.

not be capable of such a cyclization; thus, more extensive studies are needed.

Experimental

The elemental analyses were carried out by Miss S. Hirashima, of the Research Institute of Industrial Science, Kyushu University. The NMR spectra were measured by a JEOL FX 100 Spectrometer in $CDCl_3$ solution, unless otherwise specified, and the chemical shifts expressed were in δ unit. The mass spectra were measured with a JEOL OlSG-2 Spectrometer. The IR spectra were taken as either KBr disks or an inserted liquid film between NaCl plates using a Jasco IR-A 102 Spectrometer.

Preparation of 2,5-Bis(allyloxy)tropone (1). To a mixture of an anhydrous hexamethylphosphorictriamide (HMPA, 100 cm^3), **11** (2.0 g), and NaH (55%, 1.3 g), 3-bromo-1-propene (3 cm^3) was added under an N_2 atmosphere at 70 °C. After stirring for 4 h, the mixture was acidified with dil HCl and extracted with ether. A silica-gel column chromatography of the extract afforded 5-allyloxytropolone [colorless needles, mp 137—138 °C (lit,[14] 137—138 °C), 485 mg; 19%], and **1** [a colorless oil, 1.65 g; 52%].[14]

Thermal Reaction of 2,5-Bis(allyloxy)tropone (1). Formation of 2, 4, and 5. A xylene solution (50 cm^3) of **1** (1.17 g) was refluxed for 5 h under an N_2 atmosphere. The mixture was then heated in vacuo to remove the solvent, and the residue was chromatographed on a silica-gel column to give **5** [colorless needles, mp 72—73 °C (lit,[14] mp 72—73 °C), 316 mg; 27%], **4** [pale yellow crystals, mp 142.5—144.5 °C, 113 mg; 9.7%. Found: C, 71.53; H, 6.48%. Calcd for $C_{13}H_{14}O_3$: C, 71.54; H, 6.47%. ^{1}H NMR δ=3.37 (2H, d, J=5.5 Hz), 3.53 (2H, d, J=5.5 Hz), 4.9—5.3 (4H, m), 5.7—6.2 (2H, m), 7.30 (1H, br s), 7.43 (1H, s), and 8.1 (2H, br s). ^{13}C NMR δ=38.9, 39.2, 117.8, 118.0, 126.7, 128.2, 134.7, 134.9, 136.4, 138.5, 155.1, 164.5, and 167.2. IR ν: 3200—2600, 1395, 1290, 1240, and 925 cm^{-1}. UV $\lambda_{\max}^{\mathrm{MeOH}}$: 246.5 nm ($\varepsilon$=28400), 337.2 (7600), and 390 (11300)], and **2** [colorless needles, mp 126—127 °C (lit, [14] 126—127 °C), 304 mg; 26%].

Acetylation of 2 to 3. A pyridine solution (0.3 cm^3) of **2** (15 mg) was treated with Ac_2O (20 mg) at room temperature for 24 h. The mixture was evaporated in vacuo, washed with dil $NaHCO_3$, and chromatographed on a silica-gel column to give **3** [colorless needles, mp 64.5—65.5 °C (lit, [14] 64.5—65.5 °C), 14 mg; 85%. Found: C, 67.41; H, 6.07%. Calcd for $C_{17}H_{18}O_5$: C, 67.54; H, 6.00%. ^{1}H NMR δ=2.28 (6H, s), 3.40 (4H, dd, J=7, 1 Hz), 5.1—5.2 (4H, m), 5.84 (2H, m), and 7.02 (2H, t, J=1 Hz). IR ν: 2980, 1765, and 1635 cm^{-1}].

Methylation of 2. Formation of 7 and 8. A 1 : 1-mixture of ether and acetone (50 cm^3) containing **2** (129 mg) was treated with an excess of ethereal CH_2N_2 at 5—10 °C, and chromatographed on a silica-gel column to give **7** [a colorless oil, 76.4 mg; 53%. Found: M. W., 246.1214. Calcd for $C_{15}H_{18}O_3$: 246.1256. ^{1}H NMR δ=3.46 (4H, dm, J=7 Hz), 3.86 (6H, s), 5.0—5.2 (4H, m), 5.7—6.1 (2H, m), and 7.32 (2H, s). ^{13}C NMR δ=39.9 (2C), 58.9 (2C), 117.5 (2C), 129.5 (2C), 135.9 (2C), 145.8 (2C), 150.5 (2C), and 182.0. IR ν: 3500, 3080, 2990, 2950, 2850, 1735, 1710, 1635, 1560, 1490, 1390, 1255, 1130, 1090, 995, and 915 cm^{-1} UV $\lambda_{\max}^{\mathrm{MeOH}}$: 229 nm ($\varepsilon$=12200), 245 (14300), and 355 (9700)], and **8** [a colorless oil, 56.6 mg; 40%. Found: M. W., 246.1255. ^{1}H NMR δ=3.38 (2H, dm. J=7 Hz), 3.45 (2H, dm, J=7 Hz), 3.64 (3H, s), 3.85 (3H, s), 5.0—5.2 (4H, m), 5.7—6.1 (2H, m), 6.59 (1H, m), and 7.15 (1H, m). ^{13}C NMR δ=38.5, 39.4, 56.1, 61.7, 115.5, 117.7, 117.9, 134.8, 135.6, 136.4, 136.7, 147.6, 155.9, 161.2, and 178.9. IR ν: 3490, 3080, 2980, 2940, 2850, 1590, 1560, 1480, 1390, 1280, 1220, 1170, 1130, 1100, 1010, 990, and 920 cm^{-1}. UV $\lambda_{\max}^{\mathrm{MeOH}}$: 247 nm ($\varepsilon$=24900), 308 (5300, sh), 324 (7100, sh), 351 (7900), and 371 (5300)]. From the intermediary fractions, **9** [a colorless oil, a trace amount. Found: M. W., 246.1308. ^{1}H NMR δ=3.54 (2H, dt, J=6, 1.5 Hz), 3.64 (2H, dt, J=6, 1.5 Hz), 3.76 (3H, d, J=0.5 Hz), 3.81 (3H, d, J=0.5 Hz), 4.8—5.1 (4H, m), 5.7—6.1 (2H, m), 6.26 (1H, dq, J=11, 0.5 Hz), and 6.60 (1H, dq, J=11, 0.5 Hz). IR ν: 3600, 3090, 3000, 2950, 2850, 1600, 1560, 1505, 1460, 1410, 1390, 1240, 1210, 1175, 1125, and 1045 cm^{-1}. UV $\lambda_{\max}^{\text{MeOH}}$: 245 nm ($\varepsilon$=19400), 332 (6900), 362 (7100), and 379 (5400, sh)], were isolated.

Further Thermal Reaction of 5. A xylene solution (4 cm^3) of **5** (70.5 mg) was heated in a sealed tube for 12 h. Silica-gel column chromatography of the mixture afforded **4** [50.8 mg; 72%] and **6** [yellow prisms, mp 172—174 °C, 8.5 mg; 12%. Found: C, 71.66; H, 6.52%. ^{1}H NMR (CD$_3$OD) δ=3.63 (2H, dt, J=6, 2 Hz), 3.73 (2H, dt, J=6, 2 Hz), 4.95—5.1 (4H, m), 5.75—6.2 (2H, m), 7.08 (1H, d, J=12 Hz), and 7.20 (1H, d, J=12 Hz). ^{13}C NMR (CD$_3$OD) δ=35.8, 36.3, 116.0 (2C), 123.3, 123.5, 136.5 (2C), 141.0, 141.7, 158.8, 166.0, and 169.7. IR ν: 3080—2330, 1630, 1610, 1520, 1350, and 1260 cm^{-1}. $\lambda_{\max}^{\text{MeOH}}$: 246 nm ($\varepsilon$=25400), 339 (7400), 380 (9000), and 394.5 (9800)].

Methylation of 6. Similarly, **6** (21.4 mg) was methylated with ethereal CH_2N_2 to give **9** [15.3 mg; 63%], which was identical with the sample obtained from the above methylation mixture.

Methylation of 5-Hydroxytropolone. An acetone suspension (7 cm^3) of **11** (20 mg) was treated with ethereal CH_2N_2 (30 cm^3) and kept at 5 °C for 16 h. The resultant homogeneous solution was evaporated in vacuo and chromatographed on an alumina column to give 2,5-dimethoxytropone [17.5 mg; 71%] and 4,5-dimethoxytropone [colorless needles, mp 52—53 °C, 4.2 mg; 17%. Found: C, 65.11; H, 5.98%. Calcd for $C_9H_{10}O_3$: C, 65.05; H, 6.07%. ^{1}H NMR δ=3.91 (6H, s), 6.92 (2H, d, J=12 Hz), and 7.23 (2H, d, J=12Hz). ^{13}C NMR δ=58.6 (2C), 130.8 (2C), 136.3 (2C), 152.3 (2C), and 184.6].

Preparation of 5-Hydroxytropolone-3,7-d_2 (11-3,7-d_2). 2-Methoxytropone-3,5,7-d_3 (1.07 g) was dissolved in a mixed solution (260 cm^3) of MeOH:CS$_2$:ether (1:9:3) and irradiated by a 400-W tungsten lamp in the presence of tetraphenylporphyrin (42 mg) under the O_2 atmosphere at −30 °C for 10 h. The mixture was then treated with thiourea (5 g) at −5 °C for 4 d to give **11**-3,7-d_2 [665 mg; 62%].

Preparation of 2,5-Bis(2-propynyloxy)tropone-3,7-d_2 (10-d_2). An HMPA solution (5 cm^3) of **11**-3,7-d_2 (100 mg) was treated with NaH (50%, 103 mg) at room temperature, and 3-bromo-1-propyne (270 mg) was added drop by drop at room temperature. After being kept at 60 °C with stirring for 4 h, the mixture was worked up as usual to give **10**-d_2 [36 mg; 24%. ^{1}H NMR δ=2.51 (1H, t, J=2.5 Hz), 2.57 (1H, t, J=2.5 Hz), 4.65[22] (2H, d, J=2.5 Hz), 4.83 (2H. d, J=2.5 Hz), 6.43 (0.86H, br s), and 7.06 (1.14H, br s). m/z, 216:217:218:219=6.9:30.6:60.0:2.5].

Catalytic Deuteration of 10-d_2 with Lindlar's Catalyst to 1-d_6. An AcOEt solution (1.5 cm^3) with quinoline (0.25 cm^3) of **10**-d_2 (47.8 mg) was reduced by Lindlar's catalyst (Pd/CaCO$_3$–Pb, 25 mg) with D_2 gas. After take up of 13.4 cm^3 of D_2 (1.35 mol equiv), the mixture was chromatographed on a silica-gel column to give **1**-d_6 [a colorless oil, 23 mg; 46%. ^{1}H NMR δ=4.44 (2H, br s), 4.59 (2H, br s), 5.25—5.4 (1.82H, m), 6.2—6.4 (0.73H, m), 6.28 (0.24H, d, J=12 Hz), 6.76 (0.24H, d, J=12 Hz), and 6.9—7.2 (1.21H, m). m/z=220:221:222:223:224:225:226:227=14.8:4.6:2.1:4.2:8.3:23.1:25.8:17.0].

Thermal Reaction of 1-4,6-d_2. A xylene solution (6 cm^3) of **1**-4,6-d_2 [93 mg. ^{1}H NMR δ=4.44 (2H, dt, J=5, 1.5 Hz), 4.60 (2H, dt, J=5, 1.5 Hz), 5.2—5.5 (4H, m), 5.8—6.2(2H, m), 6.74 (0.38H, s), and 7.15 (0.38H, s)] was similarly thermolyzed. Silica-gel column chromatographic fractionation gave **5**-d_2 [12.5 mg. ^{1}H NMR (CD$_3$OD) δ=3.52 (2H,dt, J=6.5, 1.5 Hz), 4.52 (2H, dt, J=5, 1.5 Hz), 5.0—5.5 (4H. m), 5.7—6.2 (2H, m), and 7.26 (0.38H, s)] and **4**-d_1 [11.2 mg. ^{1}H NMR (CD$_3$OD) δ=3.35—3.65 (4H, m), 4.9—5.3 (4H, m), 5.7—6.2 (2H, m), and 7.35 (0.29H, s)], and **2**-d_0 [20 mg. ^{1}H NMR (CD$_3$OD) δ=3.35—3.55 (4H, m), 4.9—5.5 (4H, m), 5.7—6.2 (2H, m), and 7.35 (0.68H, s)].

Thermal Reaction of a 1:2-Mixture of 1-d_6 and 1-d_0. A xylene solution (5 cm^3) of 1:2-mixture of **1**-d_6 and **1**-d_0 (69 mg) was similarly refluxed for 3 h. The mixture was fractionated on a silica-gel column to give **2**-d [17.3 mg. ^{1}H NMR (CD$_3$OD) δ=3.43 (4.3H br d, J=7 Hz), 5.0—5.2 (4.5H, m), 5.7—6.2 (2H, m), and 7.35 (1.9H, s). ^{13}C NMR (CD$_3$OD) δ=39.6, 116.0, 128.7, 135.5, 141.3, and 156.9 (3C)], **4**-d [10 mg. ^{1}H NMR (CD$_3$OD) δ=3.35—3.6 (3.8H, m), 5.0—5.2 (5H, m), 5.7—6.2 (2H, m), 7.20 (0.7H, s), and 7.36 (1.3H, s). ^{13}C NMR (CD$_3$OD) δ=39.7, 40.1, 117.5 (2C), 127.7, 128.8, 136.8, 137.1, 139.4 (2C), 157.5, 166.8, and 167.8], and **5**-d [15.6 mg. ^{1}H NMR (CD$_3$OD) δ=3.50 (2H, br d, J=7 Hz). 3.82 (2.3H, dt, J=5, 1.5 Hz), 5.0—5.5 (5H, m), 5.7—6.2 (2H, m), 6.94 (1H, dd J=11.5, 3 Hz), and 7.24 (d, J=3 Hz) +7.27 (d, J=11 Hz) for 2.2H. ^{13}C NMR (CD$_3$OD) δ=39.3, 69.8, 117.7, 118.7, 120.3, 129.8, 132.4, 135.1, 140.4, 157.9, 163.1, and 171.2], respectively.

DDQ-dehydrogenation of 4 to 3,6-Diallyl-*p*-tropoquinone (12). An acetone solution (5 cm^3) of **4** (129 mg) was treated with DDQ (160 mg) at room temperature for 15 h. The mixture was then filtered off to remove the resultant hydroquinone; the filtrate was chromatographed on a silica-gel column to give **12** [a yellow oil, 117 mg; 92%. Found: M. W., 216.0817. Calcd for $C_{13}H_{12}O_3$: 216.0787. ^{1}H NMR δ=3.25 (4H, dm, J=6.5 Hz), 5.0—5.3 (4H, m), 5.68 (2H, ddt, J=16, 10.5, 6.5 Hz), 6.71 (1H, t, J=1 Hz), and 6.78 (1H, t, J=1 Hz). ^{13}C NMR δ=36.4, 37.2, 119.2, 120.0, 132.1, 132.5, 133.0, 138.1, 145.2, 151.2, 188.4, 189.6, and 189.8. IR ν: 1665, 1250, 1235, 995, and 920 cm^{-1}].

Electrolytic Conversion of 13 to 9-Allyl-7-hydroxycyclohepta[*b*]pyran-6(2*H*)-one (14). An anhydrous DMF solution (30 cm^3) of **13** (172.2 mg) was electrolyzed in the presence of TBAT (1 g) at -0.4 V for 25 h. After evaporation of the mixture in vacuo, the residue was chromatographed on a silica-gel column to give **14** [colorless crystats,mp 104—106 °C, 23 mg; 13%. Found: M. W., 216.0786. Calcd for $C_{13}H_{12}O_3$: 216.0787. ^{1}H NMR δ=3.38 (2H, dt, J=6.5, 1.5 Hz), 4.75 (2H, dd, J=3.5, 2 Hz), 5.08 (1H, dq, J=9.5, 1.5 Hz), 5.09 (1H, dq, J=17.5, 1.5 Hz), 5.92 (1H, ddt, J=17.5, 9.5, 6.5 Hz), 6.11 (1H, dt, J=9.5, 3.5 Hz), 6.37 (1H, dt, J=9.5, 2 Hz), 6.96 (1H, s), and 7.24 (1H, s). IR ν: 3450, 3200, 1595, 1582, 1512, 1445, 1230, and 1195 cm^{-1}. UV $\lambda_{\max}^{\text{MeOH}}$: 264 nm ($\varepsilon$=8900, sh), 272 (9700), 284 (6600), 318 (2200), 359 (1800), 407 (2100), and 424 (1900)].

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References

1) E. Sebe and S. Matsumoto, *Proc. Jpn. Acad.*, **29**, 207 (1953).

2) Y. Kitahara and M. Funamizu, *Bull. Chem. Soc. Jpn.*, **31**, 782 (1958); Y. Kitahara and T. Kato, *ibid.*, **37**, 895 (1964).

3) H. Takeshita, I. Kouno, and K. Miyake, *Kyushu Daigaku Seisan Kagaku Kenkyusho Hokoku,* **66**, 1 (1977); H. Takeshita, K. Tajiri, and I. Kouno, *Heterocycles,* **6**, 1101 (1977).

4) A. Pride, J. Zindely, and H. Schmid, *Helv. Chim. Acta,* **57**, 1598 (1974); R. M. Harrison, J. D. Hobson, and A. W. Midgley, *J. Chem. Soc., Perkin Trans. 1,* **1973**, 1958.

5) H. Takeshita, K. Tajiri, and I. Kouno, *Bull. Chem. Soc. Jpn.*, **52**, 223 (1979).

6) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie, GmbH., Weinheim/Bergstr. (1970), p. 114.

7) H. Takeshita, H. Mametsuka, and K. Uchida, Chem. Lett., **1982**, 1061. Even the 2-alkoxy-(or 2-cycloalkoxy)-tropones were thermolyzed via the other concerted process, to alkenes (or cycloalkenes) and tropolones. See H. Takeshita and H. Mametsuka, *J. Chem. Soc., Chem. Commun.*, **1983**, 483; *Can. J. Chem.*, **62**, 2035 (1984).

8) R. M. Harrison, J. D. Hobson, and M. M. Al Holly, *J. Chem. Soc. (C)*, **1971**, 3084.

9) H. Takeshita, H. Mametsuka, A. Chisaka, and N. Matsuo, *Chem. Lett.*, **1981**, 71.

10) H. Takeshita and H. Mametsuka, *Heterocycles,* **22**, 663 (1984).

11) H. Takeshita, H. Mametsuka, and H. Motomura, *J. Heterocyclic Chem.*, **23**, 1211 (1986).

12) H. Takeshita, A. Mori, Y. Watanabe, T. Kusaba, S. Sugiyama, and M. Kodama, in preparation.

13) H. Takeshita, H. Mametsuka, and N. Matsuo, *Bull. Chem. Soc. Jpn.*, **55**, 1137 (1982).

14) H. Takeshita, K. Tajiri, and I. Kouno, *Kyushu Daigaku Seisan Kagaku Kenkyusho Hokoku,* **70**, 65 (1979).

15) A. Mori, Y. Isayama, T. Kusaba, and H. Takeshita, *Kyushu Daigaku Sogo Rikogaku Kenkyuka Hokoku,* **3**, 125 (1981).

16) H. Takeshita, A. Mori, and Y. Goto, *Bull. Chem. Soc. Jpn.*, **59**. 1125 (1986).

17) A. Mori, T. Kusaba Y. Isayama, and H. Takeshita, *Chem. Lett.*, **1986**, 155.

18) The **11**-d_2 was prepared by heating in a sealed tube at 170—180 °C with D_2O (See H. Takeshita, T. Kusaba, and A. Mori, *Chem. Lett.*, **1982**, 701). The product was inevitably contaminated by some amounts of mono-, tri-, and tetradeuterio derivatives. The isotope distributions of **1**-d_2 prepared from this sample can be seen in Table 1.

19) The [3,7] sigmatropy has been proposed in Claisen rearrangement of 3-bromo- and 3-chloro-2-(2-propynyloxy)-tropones to 7-halo-cyclohepta[*b*]furan-8-ones. See R. M. Harrison, J. D. Hobson, and A. W. Midgley, *J. Chem. Soc., Perkin Trans. 1,* **1976**, 2403.

20) The electrolysis was carried out by Hokuto Denko Potentiostat/Galvanostat HA-301.

21) Formation of **14** from **13** constituted another structure proof for **2**.

22) Integrated peak area were calculated from the underlined standard values.