A Simple and Convenient Synthesis of 5-Alkyl-Substituted 3-Isopropenyl- and 3-Acetyltropolones

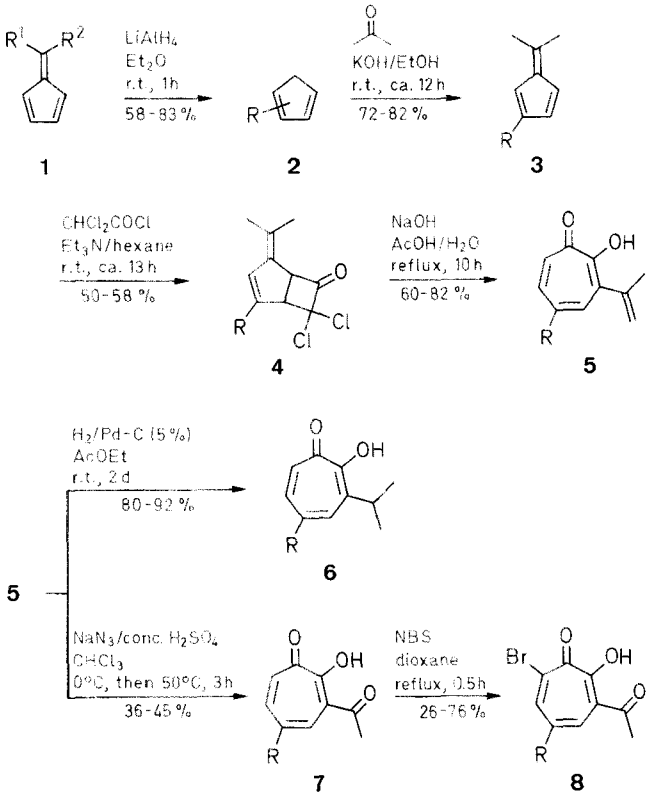
Kimiaki Imafuku,* Kiyomi Arai[1]

Department of Chemistry, Faculty of Science, Kumamoto University, Kurokami, Kumamoto 860, Japan

2-Alkyl-substituted 6,6-dimethylfulvenes **3a–d**, prepared by alkaline condensation of alkylcyclopentadienes **2a–d** with acetone, react with dichloroketene to give 2-alkyl-substituted 7,7-dichloro-4-isopropylidenebicyclo[3.2.0]hept-2-en-6-ones **4a–d**. The cycloadducts **4a–d** are hydrolyzed in aqueous acetic acid in the presence of sodium acetate to give 5-alkyl-substituted 3-isopropenyltropolones (2-hydroxy-3-isopropenyl-2,4,6-cycloheptatrienones) **5a–d**. These 3-isopropenyltropolones **5a–d** are hydrogenated on 5% palladium-charcoal to afford 5-alkyl-3-isopropyltropolones **6a–d** and treated with hydrazoic acid to give 5-alkyl-3-acetyltropolones **7a–d**.

We have reported that 3-acetyltropolone is a useful starting material for the synthesis of heterocycle-fused seven-membered aromatic compounds.[2] On the other hand, we found some pharmacological activities of 1,8-dihydrocycloheptapyrazol-8-one derivatives. In troponoid chemistry, there are many investigations not only concerning their syntheses and reactions but also with respect to their biological and pharmacological activities. It is found that an isopropyl group remarkably enhanced the antibiotic activities of hinokitiol as well as pharmacological activities of isochromanyltropolones,[3] guaiazulenes,[4] etc., and that it is as essential group for appearance of the activities. This paper deals with an introduction of alkyl group, such as the isopropyl group, to 3-acetyltropolone, which is a precursor to heterocycle-fused troponoid compounds with potentially increased pharmacological activities.

It is well-known that the tropolone nucleus is highly susceptible to various electrophilic substitution reactions, such as bromination, nitration, diazo-coupling reactions.[5–8] However, the tropolone nucleus does not undergo the Friedel–Crafts alkylation and acylation by the usual method, except for the acylation of tropone-tricarbonyliron.[9] Carbon–carbon bond formations of ring-carbon atoms in tropolones are restricted to only few reactions. Recently, the formations of carbon–carbon bond by intramolecular rearrangements have been reported.[10,11] The synthesis of some 4- and/or 5-alkyltropolones[12–15] using Stevens' procedure[16] has been reported. We investigated the introduction of an alkyl group into 3-isopropenyl- and 3-acetyltropolenes before construction of the tropolene nucleus.



1	R^1	R^2	2–8	R
a	CH_3	CH_3	a	CH_3
b	CH_3	C_2H_5	b	$CH(CH_3)_2$
c	C_2H_5	C_2H_5	c	$CH(CH_3)C_2H_5$
			d	$CH(C_2H_5)_2$

Scheme A

As starting materials, we used alkyl-substituted cyclopentadienes. Methylcyclopentadiene **(2a)** was obtained by thermal decomposition of the commercially available dimer. Isopropylcyclopentadiene **(2b)**[17] was prepared by lithium aluminum hydride reduction of 6,6-dimethylfulvene **(1a)**.[18] (2-Butyl)cyclopentadiene **(2c)** and (3-pentyl)cyclopentadiene **(2d)** were also prepared as yellow oils by reduction of 6-ethyl-6-methylfulvene **(1b)**[19] and 6,6-diethylfulvene **(1c)**,[19] respectively. Their structures were spectroscopically confirmed.

A mixture of methylcyclopentadiene **(2a)** and acetone was stirred overnight in the presence of potassium hydroxide to afford 2,6,6-trimethylfulvene **(3a)** as an orange oil. Although the position of the methyl group in the five-membered ring could not be determined from the spectral data, it was confirmed to be at the 2-position from the structure of the following cycloadduct **4a**. 2-Isopropyl- **(3b)**, 2-(2-butyl)- **(3c)**, and 2-(3-pentyl)-6,6-dimethylfulvene **(3d)** were also obtained as orange oils. Their structures were spectroscopically determined.

When triethylamine was added dropwise to a stirred mixture of 2,6,6-trimethylfulvene **(3a)** and dichloroacetyl chloride in dry hexane, generating dichloroketene *in situ*, followed [2+2] cycloaddition,[20] afforded 7,7-dichloro-4-isopropylidene-2-methylbicyclo[3.2.0]hept-2-en-6-one **(4a)** as an amber oil. In the ^{1}H-NMR spectrum of **4a**, the ring protons were assigned by analogy to those of a variety of cycloadducts.[21] Namely, the methyl group was determined to be at the 2-position. 2-Isopropyl- **(3b)**, 2-(2-butyl)- **(3c)**, and 2-(3-pentyl)-6,6-dimethylfulvene **(3d)** similarly gave the corresponding cycloadducts **4b–d**.

Keeping in mind that isomeric 1-alkyl- and 2-alkyl-6,6-dimethylfulvenes are possible due to an equilibrium between the tautomeric alkylcyclopentadienes **2a–d**, it is surprising to note that only 2-alkyl-6,6-dimethylfulvenes have been isolated. Nevertheless, it might be thought that the alkyl group was selectively fixed at the 2-position due to the steric hindrance between the alkyl group and the introduced isopropylidene group in the step **2** to **3**.

A solution of the cycloadducts **4a–d** in aqueous acetic acid was refluxed for 10 h in the presence of sodium acetate to give the hydrolyzed products, 5-alkyl-substituted 3-isopropenyltropolones **5a–d**. The methyl- and isopropyl-substituted products **5a, b** were obtained as crystals, and the 2-butyl- and 3-pentyl-substituted ones **5c, d** as oily substances. Their structures were confirmed from the spectral data and elemental analyses.

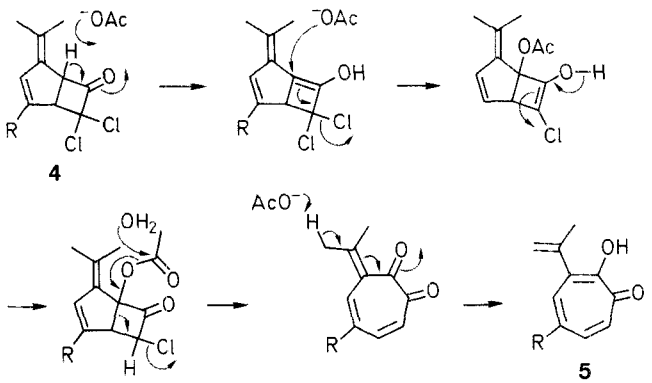
The hydrolysis of the cycloadducts **4** is explained by the mechanism via cine-substitution which was demonstrated by Bartlett,[22] as shown in Scheme **B**.

These 5-alkyl-substituted 3-isopropenyltropolones **5a–d** were hydrogenated in the presence of 5% palladium charcoal to afford the corresponding dialkyl-substituted tropolones, 5-alkyl-3-isopropyltropolones **6a–d**, as oily substances in good yields.

Table 1. Compounds **2**, **3**, and **4** Prepared

Compound	Yield (%)	bp (°C)/mbar	Molecular Formula or Lit. bp (°C)/mbar	Exact Mass *m/z* (M^+) (M^+, calc.)	MS (70 eV) *m/z* (%)	IR ($CHCl_3$) ν (cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS) δ, *J* (Hz)
2b	83	34/21	28–30/18[17]				1.13 [d, 6H, *J* = 7, $C(CH_3)_2$]; 1.84 (sept, 1H, *J* = 7, CH); 2.7–2.9 (m, 2H, CH_2); 5.8–6.5 (m, 3H)
2c	61	43–45/18	C_9H_{14} (122.2)	122.1130 (122.1095)	122 (M^+, 50); 120 (14); 107 (14); 105 (13); 93 (100)		0.83 (t, 3H, *J* = 7, 4′-CH_3); 1.10 (d, 3H, *J* = 7, 1′-CH_3); 1.43 (dm, 2H, *J* = 7, CH_2); 2.1–2.7 (m, 1H, 2′-CH); 2.7–3.1 (m, 2H, 3′-CH_2); 5.8–6.6 (m, 3H)
2d	58	61–63/20	$C_{10}H_{16}$ (136.2)	136.1222 (136.1252)	136 (M^+, 70); 134 (86); 107 (100)		0.79 [t, 6H, *J* = 7, $C(C-CH_3)_2$]; 1.41 [qm, 4H, *J* = 7, $C(CH_2)_2$]; 1.8–2.4 (m, 1H, CH); 2.75 (dm, 2H, *J* = 9, CH_2); 5.7–6.4 (m, 3H)
3a	72	79/20	C_8H_{12} (120.2)	120.0938 (120.0938)	120 (M^+, 100); 105 (83); 91 (19)	1640 (C=C)	2.08 [s, 6H, 6,6-$(CH_3)_2$]; 2.17 (s, 3H, 2-CH_3); 5.9–6.5 (m, 3H)
3b	75	105/30	$C_{11}H_{16}$ (148.2)	148.1255 (148.1252)	148 (M^+, 100); 133 (69); 105 (18); 91 (12)	1640 (C=C)	1.12 [d, 6H, *J* = 7, 2-$C(CH_3)_2$]; 2.08 [s, 6H, 6,6-$(CH_3)_2$]; 2.60 (sept, 1H, *J* = 7, 2-CH); 5.9–6.4 (m, 3H)
3c	82	112–113/25	$C_{12}H_{18}$ (162.3)	162.1393 (162.1408)	162 (M^+, 54); 147 (32); 133 (100); 119 (23); 105 (38)	1640 (C=C)	0.86 [t, 3H, *J* = 7, 2-$C(C-CH_3)$]; 1.11 [d, 3H, *J* = 7, 2-$C(CH_3)$]; 1.43 [qm, 2H, *J* = 7, 2-$C(CH_2)$]; 2.08 [s, 6H, 6,6-$(CH_3)_2$]; 2.50 (m, 1H, 2-CH); 5.9–6.4 (m, 3H)
3d	79	115–118/20	$C_{13}H_{20}$ (176.3)	176.1564 (176.1565)	176 (M^+, 70); 148 (41); 147 (100); 119 (39); 105 (43)	1640 (C=C)	0.81 [t, 6H, *J* = 7, 2-$C(CH_3)_2$]; 1.41 [qm, 4H, *J* = 7, 2-$C(CH_2)_2$]; 2.08 [s, 6H, 6,6-$(CH_3)_2$]; 2.55 (m, 1H, 2-CH); 5.9–6.35 (m, 3H)
4a	58	102–103/0.3	$C_{11}H_{12}Cl_2O$ (231.1)	230.0249 (230.0265)	234 (M^+ + 4,5); 232 (M^+ + 2, 27); 230 (M^+, 40); 197 (7); 195 (19); 189 (16); 187 (11); 169 (27); 167 (73); 141 (11); 139 (32); 120 (100); 105 (46)	1805 (C=O)[a]	1.80 [br s, 6H, 4=$C(CH_3)_2$]; 2.30 (s, 3H, 2-CH_3); 3.85 (d, 1H, *J* = 7.4, H-1); 4.68 (dm, 1H, *J* = 7.4, H-5); 6.23 (m, 1H, H-3)
4b	50	108–110/0.5	$C_{13}H_{16}Cl_2O$ (259.2)	258.0560 (258.0579)	262 (M^+ + 4, 5); 260 (M^+ + 2, 29); 258 (M^+, 42); 245 (3); 243 (5); 225 (6); 223 (17); 197 (19); 195 (52); 148 (100); 133 (69); 115 (11); 105 (11)	1805 (C=O)[a]	1.14 [d, 3H, *J* = 7, 2-$C(CH_3)$]; 1.21 [d, 3H, *J* = 7, 2-$C(CH_3)$]; 1.79 [br s, 6H, 4=$C(CH_3)_2$]; 2.7–3.0 (m, 1H, 2-CH); 4.00 (d, 1H, *J* = 8, H-5); 4.65 (m, 1H, H-1); 6.20 (m, 1H, H-3)
4c	55	115–117/1.0	$C_{14}H_{18}Cl_2O$ (273.2)	272.0739 (272.0734)	276 (M^+ + 4, 4); 274 (M^+ + 2, 25); 272 (M^+, 39); 211 (21); 209 (58); 181 (20); 162 (85); 147 (32); 134 (41); 133 (100)	1805 (C=O)[a]	0.7–1.8 (m, 8H); 1.83 [br s, 6H, 4=$C(CH_3)_2$]; 2.2–3.0 (m, 1H, 2-CH); 4.00 (d, 1H, *J* = 8, H-5); 4.65 (dm, 1H, *J* = 8, H-1); 6.22 (m, 1H, H-3)
4d	52	125–127/0.7	$C_{15}H_{20}Cl_2O$ (287.2)	286.0922 (286.0891)	290 (M^+ + 4, 8); 288 (M^+ + 2, 42); 286 (M^+, 62); 225 (30); 223 (84); 176 (65); 148 (59); 147 (100)	1805 (C=O)[a]	0.84 [t, 3H, *J* = 7, 2-$C(C-CH_3)$]; 0.96 [t, 3H, *J* = 7, 2-$C(C-CH_3)$]; 1.54 [qm, 4H, *J* = 7, 2-$C(CH_2)_2$]; 1.83 [s, 6H, 4=$C(CH_3)_2$]; 2.42 (sept, 1H, *J* = 7, 2-CH); 3.89 (d, 1H, *J* = 8, H-5); 4.66 (dm, 1H, *J* = 8, H-1); 6.20 (m, 1H, H-3)

[a] Neat.



Scheme **B**

When the 5-alkyl-3-isopropenyltropolones **5a–d** were treated with sodium azide in concentrated sulfuric acid, the corresponding 5-alkyl-substituted 3-acetyltropolones **7a–d** were obtained. 5-Methyl- and 5-isopropyl-3-acetyltropolones **(7a, b)** were obtained as crystals, and 5-(2-butyl)- and 5-(3-pentyl)-3-acetyltropolones **7c, d** as yellow oils. Their structures were determined from the spectral data and elemental analyses.

3-Acetyl-5-methyltropolone **(7a)** was brominated with *N*-bromosuccinimide (NBS) to afford 3-acetyl-7-bromo-5-methyltropolone **(8a)** as pale yellow needles. From the ^{1}H-NMR spectrum, it was reconfirmed that the methyl group was substituted at the 5-position. Similarly, 5-isopropyl-, 5-(2-butyl)- and 5-(3-pentyl)-3-acetyltropolones **(7b–d)** also gave the corresponding 7-bromo-substituted products **8b–d**

Table 2. Compounds **5** and **6** Prepared

Compound	Yield (%)	mp (°C) (solvent)	Molecular Formula	Exact Mass *m/z* (M^+) (M^+, calc.)	MS (70 eV) *m/z* (%)	IR ($CHCl_3$) ν (cm^{-1})	^{1}H-NMR ($CDCl_3$, TMS) δ, *J*(Hz)
5a	77	72–73 (hexane)	$C_{11}H_{12}O_2$[a] (176.2)		176 (M^+, 68); 175 (100); 161 (42); 133 (5); 115 (5); 105 (10)	3450 (OH), 1620 (C=O)	2.13 [d, 3H, *J* = 1.2, 3-C(CH$_3$)]; 2.43 (s, 3H, 5-CH$_3$); 5.07 [m, 1H, 3-C=CH-(*E*)]; 5.25 [m, 1H, 3-C=CH-(*Z*)]; 7.28 (br s, 2H, H-6, H-7); 7.43 (br s, 1H, H-4); 8.9 (br, 1H, OH)
5b	63	46–47 (EtOH/H_2O)	$C_{13}H_{18}O_2$[a] (204.3)		204 (M^+, 72); 203 (100); 189 (37); 174 (5); 161 (12)	3450 (OH), 1620 (C=O)	1.25 [d, 6H, *J* = 7, 5-C(CH$_3$)$_2$]; 2.15 [br s, 3H, 3-C(CH$_3$)]; 2.85 (sept, 1H, *J* = 7, 5-CH); 5.07 [m, 1H, 3-C=CH-(*E*)]; 5.25 [m, 1H, 3-C=CH-(*Z*)]; 7.30 (br s, 2H, H-6, H-7); 7.43 (br s, 1H, H-4); 9.0 (br s, 1H, OH)
5c	60	oil	$C_{14}H_{18}O_2$ (218.3)	218.1325 (218.1307)	218 (M^+, 74); 217 (100); 203 (37); 178 (20); 161 (26); 149 (33); 121 (19)	3450 (OH), 1620 (C=O)	0.81 [t, 6H, *J* = 7, 5-C(C–CH$_3$)$_2$]; 1.1–1.9 [m, 4H, 5-C(CH$_2$)$_2$]; 2.08 [s, 3H, 3-C(CH$_3$)]; 2.27 (sept, 1H, *J* = 7, 5-CH); 4.97 [m, 1H, 3-C=CH-(*E*)]; 5.12 [m, 1H, 3-C=CH-(*Z*)]; 7.0–7.2 (m, 2H, H-6, H-7); 7.32 (br s, 1H, H-4); 8.9 (br, 1H, OH)
5d	82	oil	$C_{15}H_{20}O_2$ (232.3)	232.1470 (232.1463)	232 (M^+, 70); 231 (100); 217 (32); 203 (10); 187 (13); 163 (13)	3450 (OH), 1620 (C=O)	0.81 [t, 6H, *J* = 7, 5-C(C–CH$_3$)$_2$]; 1.1–1.9 [m, 4H, 5-C(CH$_2$)$_2$]; 2.08 [s, 3H, 3-C(CH$_3$)]; 2.27 (sept, 1H, *J* = 7, 5-CH); 4.97 [m, 1H, 3-C=CH-(*E*)]; 5.12 [m, 1H, 3-C=CH-(*Z*)]; 7.0–7.2 (m, 2H, H-6, H-7); 7.32 (br s, 1H, H-4); 8.9 (br, 1H, OH)
6a	89	oil	$C_{11}H_{14}O_2$ (178.2)	178.1019 (178.0994)	178 (M^+, 65); 176 (27); 175 (34); 163 (100); 161 (22); 150 (32); 135 (26)	3450 (OH), 1615 (C=O)	1.24 [d, 6H, *J* = 7, 3-C(CH$_3$)$_2$]; 2.43 (s, 3H, 5-CH$_3$); 3.73 (sept, 1H, *J* = 7, 3-CH); 6.9–7.3 (m, 2H, H-6, H-7); 7.35 (br s, 1H, H-4); 8.5 (br, 1H, OH)
6b	92	oil	$C_{13}H_{18}O_2$ (206.3)	206.1299 (206.1307)	206 (M^+, 71); 204 (22); 203 (31); 191 (100); 178 (40); 163 (89)	3450 (OH), 1620 (C=O)	1.26 [d, 12H, *J* = 7, 3, 5-{C(CH$_3$)$_2$}$_2$]; 2.90 (sept, 1H, *J* = 7, 5-CH); 3.73 (sept, 1H, *J* = 7, 3-CH); 7.15–7.3 (m, 2H, H-6, H-7); 7.4 (br s, 1H, H-4); 8.1 (br, 1H, OH)
6c	85	oil	$C_{14}H_{20}O_2$ (220.3)	220.1450 (220.1463)	220 (M^+, 77); 205 (76); 192 (39); 191 (62); 163 (100)	3500 (OH), 1620 (C=O)	0.5–1.2 [m, 6H, 5-C(CH$_3$) + 5-C(C–CH$_3$)]; 1.24 [d, 6H, *J* = 7, 3-C(CH$_3$)$_2$]; 1.3–2.2 [m, 2H, 5-C(CH$_2$)]; 2.3–2.7 (m, 1H, 5-CH); 3.69 (sept, 1H, *J* = 7, 3-CH); 7.0–7.4 (m, 3H, H-4, H-6, H-7); 8.2 (br, 1H, OH)
6d	80	oil	$C_{15}H_{22}O_2$ (234.3)	234.1612 (234.1620)	234 (M^+, 85); 219 (52); 206 (49); 205 (100); 193 (26); 177 (86); 169 (33); 163 (50)	3500 (OH), 1620 (C=O)	0.78 [tm, 6H, *J* = 7, 5-C(C–CH$_3$)$_2$]; 1.24 [d, 6H, *J* = 7, 3-C(CH$_3$)$_2$]; 1.2–1.9 [m, 4H, 5-C(CH$_2$)$_2$]; 3.70 (sept, 1H, *J* = 7, 3-CH); 6.9–7.4 (m, 3H, H-4, H-6, H-7); 8.1 (br, 1H, OH)

[a] Satisfactory microanalyses obtained: C ±0.22, H ±0.14.

Previously, syntheses of alkyl-substituted tropolones from alkylcyclopentadienes have been reported.[12-15] Two isomeric tropolones bearing alkyl groups at the 4- and 5-position were obtained from isomerization of alkylcyclopentadienes. The present method gave 3-isopropenyl- **(5a–d)**, 3-isopropyl- **(6a–d)**, and 3-acetyltropolones **(7a–d)** bearing the alkyl group selectively at the 5-position due to the fixed position of the alkyl group in the fulvenes **3a–d**. It was found that this method is very simple and useful for the 5-alkyltropolones bearing various carbon substituents. Furthermore, these 5-alkyl-substituted 3-acetyltropolones **7a–d** are expected to be useful starting materials for pharmacologically interesting heterocycle-fused troponoid compounds bearing the alkyl group.

The melting points were determined with a Yanagimoto MP-S2 apparatus and are uncorrected. The IR spectra were taken on a JASCO A-102 spectrophotometer. The ^{1}H-NMR spectra were recorded with a JEOL JNM-PMX60SI spectrometer (60 MHz). The MS spectra were measured on a JEOL JMX-DX303HF spectrometer.

Preparation of Alkyl-Substituted Cyclopentadienes 2b–d; General Procedure:

To a stirred suspension of $LiAlH_4$ (19 g, 0.5 mol) in dry Et_2O (200 mL) is dropwise added the fulvene **1b–d** (0.5 mol) in a period of 30 min under nitrogen atmosphere. The mixture is stirred for 1 h. The excess of $LiAlH_4$ is decomposed with EtOAc (150 mL). After adding 6 M HCl (300 mL), the organic layer is separated, and the aqueous layer is extracted with Et_2O (2 × 100 mL). The combined ethereal solution is washed with H_2O (2 × 100 mL) and dried over Na_2SO_4. After removal of the solvent, the residue is distilled under reduced pressure to give the alkylcyclopentadiene **2b–d**.

Preparation of 2-Alkyl-Substituted 6,6-Dimethylfulvenes 3a–d; General Procedure:

The alkylcyclopentadiene **2a–d** (0.5 mol) and acetone (50 g, 1.0 mol) is added to a stirred solution of KOH (5.6 g, 0.1 mol) in EtOH (25 mL). The stirring is continued overnight. The mixture is washed with 1 M HCl (2 × 100 mL), H_2O (2 × 100 mL), and brine (100 mL). The organic layer is distilled under reduced pressure to give the 2-alkyl-6,6-dimethylfulvene **3a–d**.

Preparation of 2-Alkyl-Substituted 7,7-Dichloro-4-isopropylidenebicyclo[3.2.0]hept-2-en-6-ones 4a–d; General Procedure:

To a stirred solution of 2-alkyl-6,6-dimethylfulvene **3a–d** (0.5 mol) and dichloroacetyl chloride (74 g, 0.5 mmol) in dry hexane (300 mL) is added dropwise a solution of Et_3N (101 g, 1.0 mol) in dry hexane (150 mL) in a period of 3 h. The mixture is stirred for an additional 1 h and allowed to stand overnight. The reaction mixture is filtered. The filtrate is washed with 1 M HCl (2 × 100 mL), H_2O (2 × 100 mL), and brine (100 mL). After removal of the solvent, the residue is distilled under vacuum to give the 2-alkyl-7,7-dichloro-4-isopropylidenebicyclo[3.2.0]hept-2-en-6-one **4a–d**.

Table 3. Compounds **7** and **8** Prepared

Compound	Yield (%)	mp (°C) (solvent)	Molecular Formula	Exact Mass *m/z* (M^+) (M^+, calc.)	MS (70 eV) *m/z* (%)	IR ($CHCl_3$) ν (cm^{-1})	^{1}H-NMR ($CDCl_3$/TMS) δ, *J* (Hz)
7a	45	136–137 (MeOH)	$C_{10}H_{10}O_3$[a] (178.2)		178 (M^+, 71); 163 (7); 150 (37); 135 (100); 197 (22)	3500 (OH), 3175 (OH), 1690 (C=O), 1615 (C=O)	2.46 (s, 3H, 5-CH_3); 2.66 (s, 3H, $COCH_3$); 7.37 (br s, 2H, H-6, H-7); 7.65 (s, 1H, H-4); 8.1 (br, 1H, OH)
7b	43	69–70 (MeOH)	$C_{12}H_{14}O_3$[a] (206.2)		206 (M^+, 56); 191 (10); 178 (14); 163 (100); 149 (14); 145 (12)	3525 (OH), 3175 (OH), 1690 (C=O), 1615 (C=O)	1.26 [d, 6H, *J* = 7, 5-C(CH_3)$_2$]; 2.68 (s, 3H, $COCH_3$); 3.16 (d, 1H, *J* = 7, 5-CH); 7.39 (br s, 2H, H-6, H-7); 7.67 (br s, 1H, H-4); 8.7 (br, 1H, OH)
7c	36	oil	$C_{13}H_{16}O_3$ (220.3)	220.1101 (220.1100)	220 (M^+, 67); 217 (20); 191 (36); 178 (71); 163 (100); 149 (90); 121 (59)	3545 (OH), 3175 (OH), 1690 (C=O), 1615 (C=O)	0.83 [t, 3H, *J* = 7, 5-C(C–CH_3)]; 1.15 [d, 3H, *J* = 7, 5-C(CH_3)]; 1.59 [dt, 2H, *J* = 7,7, 5-C(CH_2)]; 2.3–2.9 (m, 1H, 5-CH); 2.63 (s, 3H, $COCH_3$); 7.1–7.4 (m, 2H, H-6, H-7); 7.55 (br s, 1H, H-4); 9.0 (br, 1H, OH)
7d	41	oil	$C_{14}H_{18}O_3$ (234.3)	234.1265 (234.1256)	234 (M^+, 32); 205 (27); 192 (59); 177 (46); 164 (21); 163 (100); 161 (34); 107 (33)	3550 (OH), 3180 (OH), 1690 (C=O), 1615 (C=O)	0.79 [t, 6H, *J* = 7, 5-C(C–CH_3)$_2$]; 1.1–1.9 [m, 4H, 5-C(CH_2)$_2$]; 2.0–2.9 (m, 1H, 5-CH); 2.64 (s, 3H, $COCH_3$); 7.2–7.4 (m, 2H, H-6, H-7); 7.53 (br s, 1H, H-4); 8.90 (br, 1H, OH)
8a	76	119–121 (MeOH)	$C_{10}H_9BrO_3$[a] (257.1)			3500 (OH), 3130 (OH), 1695 (C=O), 1605 (C=O)	2.47 (s, 3H, 5-CH_3); 2.67 (s, 3H, $COCH_3$); 7.50 (d, 1H, *J* = 1.6, H-6); 8.07 (d, 1H, *J* = 1.6, H-4); 8.3 (br, 1H, OH)
8b	54	121–122 (MeOH)	$C_{12}H_{13}BrO_3$[a] (285.1)			3500 (OH), 3140 (OH), 1695 (C=O), 1605 (C=O)	1.23 [d, 6H, *J* = 7, 5-C(CH_3)$_2$]; 2.67 (s, 3H, $COCH_3$); 3.05 (sept, 1H, *J* = 7, 5-CH); 7.59 (d, 1H, *J* = 1.5, H-6); 8.08 (d, 1H, *J* = 1.5, H-4); 8.5 (br, 1H, OH)
8c	26	92–94 (cyclohexane)	$C_{13}H_{15}BrO_3$[a] (299.2)			3550 (OH), 3150 (OH), 1695 (C=O), 1605 (C=O)	0.85 [t, 3H, *J* = 7, 5-C(C–CH_3)]; 1.23 [d, 3H, *J* = 7, 5-C(CH_3)]; 2.3–2.7 (m, 1H, 5-CH); 2.62 (s, 3H, $COCH_3$); 7.39 (d, 1H, *J* = 1.8, H-6); 7.90 (d, 1H, *J* = 1.8, H-4); 8.6 (br, 1H, OH)
8d	39	oil	$C_{14}H_{17}BrO_3$ (313.2)	312.0398 (312.0361)		3525 (OH), 3150 (OH), 1695 (C=O), 1605 (C=O)	0.80 [t, 6H, *J* = 7, 5-C(C–CH_3)$_2$]; 1.1–2.0 [m, 4H, 5-C(CH_2)$_2$]; 2.0–2.6 (m, 1H, 5-CH); 2.62 (s, 3H, $COCH_3$); 7.39 (d, 1H, *J* = 1.8, H-6); 7.90 (d, 1H, *J* = 1.8, H-4); 8.3 (br, 1H, OH)

[a] Satisfactory microanalyses obtained: C ±0.27, H ±0.08.

Preparation of 5-Alkyl-Substituted 3-Isopropenyltropolones 5a–d; General Procedure:

To a solution of NaOH (50 g, 1.25 mol) in AcOH (250 mL) and H_2O (25 mL) is added the 5-alkyl-substituted cycloadduct **4a–d** (0.25 mol). The mixture is refluxed for 10 h and steam-distilled. The distillate is extracted with $CHCl_3$ (3 × 100 mL). The extract is washed with aq. saturated $NaHCO_3$ (2 × 50 mL), H_2O (2 × 100 mL), and brine (100 mL), and dried over Na_2SO_4. After removal of the solvent, the residue is recrystallized to give 5-alkyl-3-isopropenyltropolone **5a, b**. The oily products **5c, d** are purified by chromatography on a column (Kieselgel 60G) with $CHCl_3$.

Hydrogenolysis of 5-Alkyl-Substituted 3-Isopropenyltropolones 5a–d; General Procedure:

A solution of 5-alkyl-3-isopropenyltropolone **5a–d** (5 mmol) in EtOAc (20 mL) is stirred for 2 d in the presence of 5% Pd-C (300 mg) under hydrogen atmosphere. After filtration of the catalyst, the residue from evaporation of the filtrate is chromatographed on a column (Kieselgel 60G) with $CHCl_3$ to give the 5-alkyl-3-isopropyltropolone **6a–d**.

Preparation of 5-Alkyl-Substituted 3-Acetyltropolones 7a–d; General Procedure:

To a solution of the 5-alkyl-3-isopropenyltropolone **5a–d** (0.25 mol) in $CHCl_3$ (100 mL) is added NaN_3 (33 g, 0.5 mol) and conc. H_2SO_4 (110 mL) in an ice-cooled bath. The mixture is warmed up to 50 °C and stirred for 3 h at the same temperature. After adding H_2O (600 mL), the solvent is evaporated under reduced pressure. The precipitate from the aqueous layer is collected and recrystallized to afford 5-alkyl-3-acetyltropolone **7a, b**. The oily products **7c, d** are purified by chromatography on a column (Kieselgel 60G) with $CHCl_3$.

Bromination of 5-Alkyl-Substituted 3-Acetyltropolones 7a–d; General Procedure:

A mixture of 5-alkyl-3-acetyltropolone **7a–d** (2.0 mmol) and NBS (356 mg, 2.0 mmol) in dioxane (5 mL) is heated at reflux for 30 min on a water bath. After adding H_2O (50 mL), the precipitate is collected and recrystallized to give 5-alkyl-3-acetyl-7-bromotropolone **8a–c**. The oily product **8d** is purified by chromatography on a column (Kieselgel 60G) with $CHCl_3$.

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(1) Present address: NEC Kyushu Ltd., Yahata-machi, Kumamoto 861-41, Japan.
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