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# 7,7-Dimethyltricyclo[3.3.0.0$^{2,8}$]octan-3-ones as Synthetic Intermediates. III.[1] Total Synthesis of (±)-Descarboxyquadrone[2]

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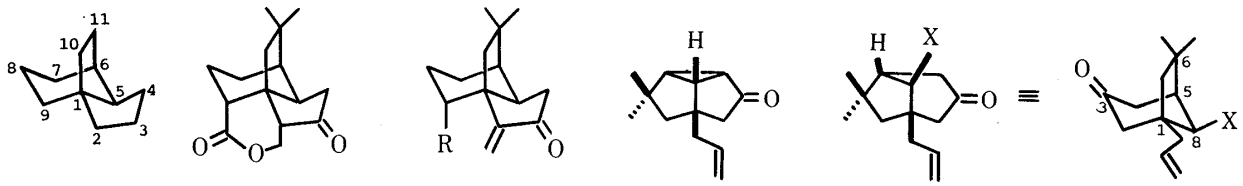
A total synthesis of (±)-descarboxyquadrone (**5**) starting from a bicyclo[3.2.1]octane (**7**; X=OH) is described. By a several-step sequence, the starting material was converted to a tricyclic compound (**18**), which was transformed to the target molecule, (±)-descarboxyquadrone (**5**), *via* a methoxymethylation.

**Keywords**——antitumor activity; descarboxyquadrone; bicyclo[3.2.1]octane; tricyclo-[4.3.2.0$^{1,5}$]undecane; total synthesis; cyclopropane ring opening

Several natural products possess a unique carbon framework, tricyclo[4.3.2.0$^{1,5}$]undecane (octahydro-3a,7-ethano-3a*H*-indene) (**1**). The representative sesquiterpene quadrone (**2**) was first isolated as a metabolite of the fungus *Aspergillus terreus* in 1978 and shows a significant antitumor activity.[3] Its congeners, terrecyclic acid A (**3**)[4] and terrecyclol (**4**),[5] were later found to have antibiotic activity. On the other hand, Smith *et al.* synthesized the decarboxy analogue (**5**) of quadrone in 1982 and found that this simple compound also showed an antitumor activity equivalent to that of quadrone itself.[6,7] These interesting structural and biological features have created a demand for reactions which may be used to form the ring system of **1**. To date, some elegant strategies for construction of **1** have been developed.[8]

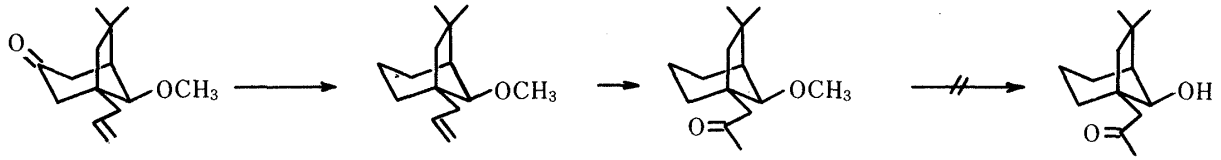
Recently we reported that a tricyclo[3.3.0.0$^{2,8}$]octan-3-one (**6**) gave a bicyclo[3.2.1]octane derivative (**7**) in substitutional reactions.[9] This conversion reaction could serve as a convenient tool for construction of the ring system of **1**. In this paper we describe a facile synthesis of (±)-descarboxyquadrone (**5**) starting from the bicyclo[3.2.1]octan-3-one (**7**; X=OH).

Initially, 8-methoxy-6,6-dimethyl-1-(2-propenyl)bicyclo[3.2.1]octan-3-one (**7**; X=OMe) was used as a starting material because this compound was obtainable more efficiently than the 8-hydroxy analogue (**7**; X=OH).[9] The modified Wolff–Kishner reduction of **7** (X=OMe)



**1** **2** **3**: R=COOH; **4**: R=$CH_2OH$; **5**: R=H **6** **7**

Chart 1

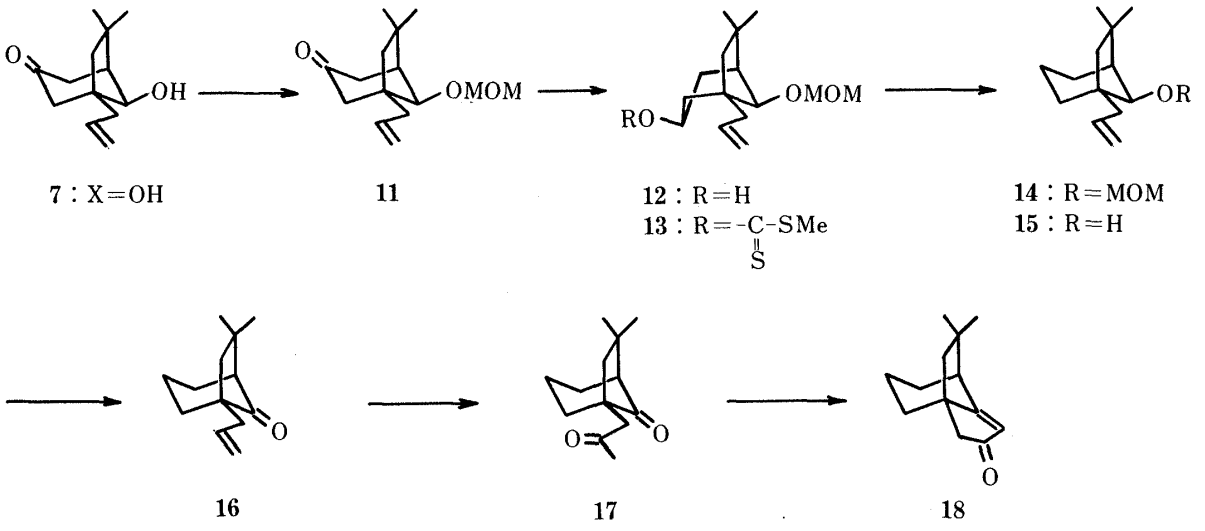



7 : X=$OCH_3$ 8 9 10

Chart 2

gave **8** in 67% yield, and **8** was subjected to oxidation under typical Wacker–Hoechst conditions, *i.e.*, it was treated with oxygen, palladium (II) chloride, and copper (I) chloride in aqueous *N*,*N*-dimethylformamide (DMF) to afford the methyl ketone (**9**) in 63% yield. In order to cleave the ether linkage of **9** several conditions were employed. All the attempts, however, failed to yield the desired product (**10**). Therefore, this route was abandoned.

Reaction of **7** (X=OH) with chloromethyl methyl ether (MOMCl) in the usual manner afforded the ether (**11**) in 93% yield. In order to reduce the carbonyl group to methylene, **11** was initially treated with sodium borohydride to give the alcohol (**12**), the cyclohexane ring of which should exist in a boat form, in 89% yield. The xanthate (**13**), obtained in 79% yield from **12** in the usual manner, was reduced with tri-*n*-butyltin hydride in benzene in the presence of 2,2′-azobisisobutyronitrile (AIBN)[10] to afford the desired compound (**14**) in 90% yield. An acidic hydrolysis of **14** to the alcohol (**15**, 77%) followed by the Jones oxidation provided the ketone (**16**, 75%), which was subjected to the Wacker–Hoechst oxidation to give the diketone (**17**) in 69% yield. Its cyclization with potassium *tert*-butoxide in *tert*-butanol under reflux afforded the tricyclic derivative (**18**) in 81% yield. Compound **18** has already been transformed into (±)-descarboxyquadrone (**5**) *via* a hydroxymethylation by Smith *et al.*[6] The hydroxymethylation[11] of **18**, however, did not give a satisfactory result in our hands.[12] Therefore, an alternative method was examined.

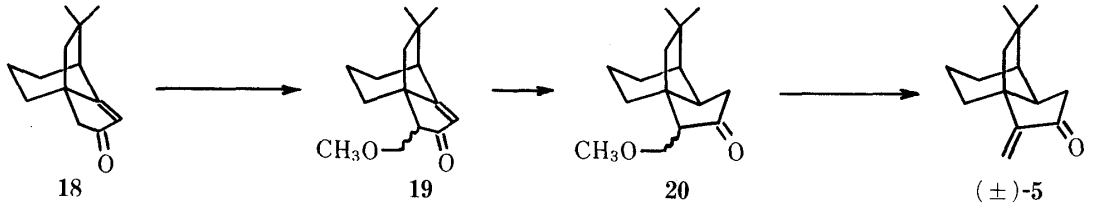



7 : X=OH 11 12 : R=H 13 : R=-C(=S)-SMe 14 : R=MOM 15 : R=H

16 17 18

Chart 3

The lithium enolate of **18** was quenched with MOMCl in tetrahydrofuran (THF), resulting in easy formation of the α-methoxymethylated ketone (**19**) in 67% yield. The proton nuclear magnetic resonance ($^1$H-NMR) spectrum of **19** indicated that the product might be a single diastereoisomer. Catalytic hydrogenation of **19** over 5% palladium on charcoal gave the saturated ketone (**20**, 88%), which was finally treated with *p*-toluenesulfonic acid (TSA) in benzene at 45 °C to afford (±)-descarboxyquadrone (**5**). Compound (±)-**5** thus obtained was found to be identical with an authentic sample[6] by means of spectral comparison.




18 19 20 (±)-5

Chart 4

## Experimental

The infrared (IR) spectra were recorded with a Hitachi 260-10 spectrometer. $^1$H-NMR spectra were measured with a Hitachi R-22 (90 MHz), a JEOL FX-90Q (90 MHz), or a JNM-GX500 (500 MHz), and the chemical shifts are given as $\delta$ (ppm) values with tetramethylsilane as an internal standard. The ultraviolet (UV) spectra were recorded with a Hitachi 124 spectrometer. The mass spectra (MS) and high-resolution MS (High MS) were obtained with a Shimadzu QP-1000 or a JEOL JMS-D300 mass spectrometer. For column chromatography, Silica gel 60 (E. Merck AG, Darmstadt) was used. After drying over anhydrous sodium sulfate or magnesium sulfate, all organic extracts were concentrated under reduced pressure.

**(1*RS*,8*SR*)-8-Methoxy-6,6-dimethyl-1-(2-propenyl)bicyclo[3.2.1]octane (8)**——A mixture of **7** (X=OMe) (97 mg, 0.44 mmol), 85% hydrazine hydrate (150 mg, 2.5 mmol), 85% KOH (300 mg, 4.5 mmol), and triethylene glycol (3 ml) was heated with stirring at 130 °C for 30 min. The reaction temperature was gradually raised to 200 °C during 3 h and stirring was continued for 5 h at this temperature. After cooling, water (20 ml) was added and the resulting mixture was extracted with ether. The extract was washed with brine, dried, and concentrated. The residue was chromatographed on silica gel with hexane to give **8** (61 mg, 67%) as a pale yellow oil. IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 3075, 1110, 995, 910. $^1$H-NMR (90 MHz, $CCl_4$) $\delta$: 1.05 (3H, s, 6-$CH_3$), 1.17 (3H, s, 6-$CH_3$), 2.95 (1H, s, 8-H), 3.18 (3H, s, $OCH_3$), 4.7—5.1 (2H, m, CH=C$\underline{H}_2$), 5.3—6.0 (1H, m, C$\underline{H}$=$CH_2$). MS *m/z* (%): 208 ($M^+$, 2.0), 109 (100). High MS Calcd for $C_{14}H_{24}O$: 208.1827. Found: 208.1834.

**(1*RS*,8*RS*)-8-Methoxy-6,6-dimethyl-1-(2-oxopropyl)bicyclo[3.2.1]octane (9)**——A stream of oxygen was bubbled into a vigorously stirred mixture of **8** (126 mg, 0.60 mmol), CuCl (0.10 g, 1.0 mmol), $PdCl_2$ (0.040 g, 0.23 mmol), water (0.2 ml), and DMF (1.5 ml) at room temperature for 20 h. After dilution with water, the reaction mixture was acidified with concentrated HCl and extracted with ether. The extract was washed with saturated $NaHCO_3$ and brine, dried, and concentrated. The residue was chromatographed on silica gel with benzene and AcOEt–hexane (1 : 5) to give **9** (85 mg, 63%) as a colorless oil. IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 1720, 1110. $^1$H-NMR (90 MHz, $CCl_4$) $\delta$: 1.06 (3H, s, 6-$CH_3$), 1.14 (3H, s, 6-$CH_3$), 1.99 (3H, s, $COCH_3$), 2.36 (1H, d, $J$=16 Hz, 1-$CH_2$), 2.62 (1H, d, $J$=16 Hz, 1-$CH_2$), 3.16 (3H, s, $OCH_3$), 3.21 (1H, s, 8-H). MS *m/z* (%): 224 ($M^+$, 13), 135 (100). High MS Calcd for $C_{14}H_{24}O_2$: 224.1777. Found: 224.1782.

**(1*RS*,8*SR*)-8-Methoxymethoxy-6,6-dimethyl-1-(2-propenyl)bicyclo[3.2.1]octan-3-one (11)**——A mixture of **7** (X=OH) (152 mg, 0.73 mmol), iso-$Pr_2NEt$ (142 mg, 1.1 mmol), MOMCl (88 mg, 1.1 mmol), and dry $CH_2Cl_2$ (3 ml) was stirred at room temperature for 12 h. The reaction mixture was diluted with $CHCl_3$ and the resulting organic layer was washed with saturated $NaHCO_3$ and brine. The dried organic layer was concentrated to leave an oil, which was chromatographed on silica gel with hexane–AcOEt (10 : 1) to give **11** (171 mg, 93%) as a colorless oil. IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 3075, 1720, 1640, 990, 920. $^1$H-NMR (90 MHz, $CCl_4$) $\delta$: 0.93 (3H, s, 6-$CH_3$), 1.20 (3H, s, 6-$CH_3$), 1.43 (1H, d, $J$=13 Hz, 7-H), 1.71 (1H, d, $J$=13 Hz, 7-H), 3.34 (3H, s, $OCH_2OC\underline{H}_3$), 3.91 (1H, s, 8-H), 4.55 (1H, d, $J$=6 Hz, $OC\underline{H}_2OCH_3$), 4.69 (1H, d, $J$=6 Hz, $OC\underline{H}_2OCH_3$), 4.8—5.1 (2H, m, CH=C$\underline{H}_2$), 5.1—5.9 (1H, m, C$\underline{H}$=$CH_2$). MS *m/z* (%): 252 ($M^+$, 1.3), 69 (100). High MS Calcd for $C_{15}H_{24}O_3$: 252.1722. Found: 252.1709.

**(1*RS*,3*RS*,8*SR*)-8-Methoxymethoxy-6,6-dimethyl-1-(2-propenyl)bicyclo[3.2.1]octan-3-ol (12)**——A large excess (*ca.* 20 eq) of $NaBH_4$ was added to a stirred solution of **11** (171 mg, 0.68 mmol) in methanol (5 ml) at 0 °C and the resulting mixture was stirred at room temperature for 30 min. The solvent was evaporated off, and the residue was extracted with $CHCl_3$. The extract was washed with brine, dried, and concentrated to leave an oil, which was chromatographed on silica gel with hexane–AcOEt (5 : 1) to give **12** (153 mg, 89%) as a colorless oil. IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 3615, 3420, 3075, 1640, 995, 915. $^1$H-NMR (90 MHz, $CCl_4$) $\delta$: 1.20 (3H, s, 6-$CH_3$), 1.23 (3H, s, 6-$CH_3$), 3.30 (3H, s, $OCH_2OC\underline{H}_3$), 3.41 (1H, s, 8-H), 3.96 (1H, m, $W_{1/2}$=14 Hz, 3-H), 4.47 (1H, d, $J$=7 Hz, $OC\underline{H}_2OCH_3$), 4.60 (1H, d, $J$=7 Hz, $OC\underline{H}_2OCH_3$), 4.8—5.2 (2H, m, CH=C$\underline{H}_2$), 5.4—6.0 (1H, m, C$\underline{H}$=$CH_2$). MS *m/z* (%): 254 ($M^+$, 1.0), 209 (100). High MS Calcd for $C_{15}H_{26}O_3$: 254.1882. Found: 254.1883.

***O*-[(1*RS*,3*RS*,8*SR*)-8-Methoxymethoxy-6,6-dimethyl-1-(2-propenyl)bicyclo[3.2.1]octan-3-yl] *S*-Methyl Dithiocarbonate (13)**——A suspension of **12** (261 mg, 1.0 mmol), NaH (60% in mineral oil, 410 mg, 10 mmol), imidazole (70 mg, 1.0 mmol), and $CS_2$ (316 mg, 4.1 mmol) in dry THF (5 ml) was stirred at 50 °C for 2 h. Then MeI (1.46 g, 10 mmol) was added to the cooled suspension and the resulting mixture was further stirred at room temperature for 30 min. Saturated aqueous $NH_4Cl$ solution was added and the whole mixture was extracted with AcOEt. The extract was washed with brine, dried, and concentrated. The oily residue was chromatographed on silica

gel with hexane and hexane–benzene (1 : 1) to give **13** as a colorless oil. IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 3075, 1640, 995, 915. $^1$H-NMR (90 MHz, $CCl_4$) $\delta$: 1.15 (3H, s, 6-$CH_3$), 1.25 (3H, s, 6-$CH_3$), 2.53 (3H, s, $SCH_3$), 3.31 (3H, s, $OCH_2OCH_3$), 3.47 (1H, s, 8-H), 4.49 (1H, d, $J$=6 Hz, $OCH_2OCH_3$), 4.63 (1H, d, $J$=6 Hz, $OCH_2OCH_3$), 4.7—5.1 (2H, m, $CH=CH_2$), 5.4—6.0 (2H, m, 3-H and $CH=CH_2$). MS $m/z$ (%): 344 ($M^+$, 0.26), 299 (0.57), 205 (100). High MS Calcd for $C_{17}H_{28}O_3S_2$–$CH_2OCH_3$: 299.1140. Found: 299.1158.

**(1*RS*,8*SR*)-8-Methoxymethoxy-6,6-dimethyl-1-(2-propenyl)bicyclo[3.2.1]octane (14)**——A mixture of **13** (125 mg, 0.36 mmol), *n*-$Bu_3SnH$ (119 mg, 0.41 mmol), AIBN (trace), and dry benzene (5 ml) was heated under reflux with stirring for 2.5 h. The solvent was evaporated off, and the residue was chromatographed on silica gel with hexane–benzene (2 : 1) to give **14** (78 mg, 90%) as a colorless oil. IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 3075, 1640, 995, 915. $^1$H-NMR (90 MHz, $CCl_4$) $\delta$: 1.08 (3H, s, 6-$CH_3$), 1.21 (3H, s, 6-$CH_3$), 2.20 (2H, d, $J$=7 Hz, 1-$CH_2$), 3.29 (3H, s, $OCH_2OCH_3$), 3.37 (1H, s, 8-H), 4.46 (1H, d, $J$=6 Hz, $OCH_2OCH_3$), 4.60 (1H, d, $J$=6 Hz, $OCH_2OCH_3$), 4.7—5.1 (2H, m, $CH=CH_2$), 5.4—6.1 (1H, m, $CH=CH_2$). MS $m/z$ (%): 238 ($M^+$, 0.9), 109 (100). High MS Calcd for $C_{15}H_{26}O_2$: 238.1933. Found: 238.1959.

**(1*RS*,8*SR*)-6,6-Dimethyl-1-(2-propenyl)bicyclo[3.2.1]octan-8-ol (15)**——A mixture of **14** (58 mg, 0.24 mmol) 10% HCl (0.5 ml), and acetone (1 ml) was stirred at room temperature for 48 h. The acetone was evaporated off, and the residue was extracted with AcOEt. The extract was washed with brine, dried, and concentrated to leave an oil, which was chromatographed on silica gel with hexane–benzene (1 : 1) to give **15** (36 mg, 77%) as a colorless oil. IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 3620, 3075, 1640, 1000, 915. $^1$H-NMR (90 MHz, $CCl_4$) $\delta$: 1.07 (3H, s, 6-$CH_3$), 1.26 (3H, s, 6-$CH_3$), 2.19 (2H, d, $J$=8 Hz, 1-$CH_2$), 3.52 (1H, s, 8-H), 4.7—5.1 (2H, m, $CH=CH_2$), 5.4—6.0 (1H, m, $CH=CH_2$). MS $m/z$ (%): 194 ($M^+$, 5.8), 109 (100). High MS Calcd for $C_{13}H_{22}O$: 194.1671. Found: 194.1686.

**6,6-Dimethyl-1-(2-propenyl)bicyclo[3.2.1]octan-8-one (16)**——The Jones reagent (8 N) was added dropwise to a stirred solution of **15** (35 mg, 0.18 mmol) in purified acetone (1 ml) under ice cooling until the color of the reagent did not disappear within a few minutes. The resulting mixture was further stirred for 20 min and iso-PrOH was added in order to decompose the excess reagent. After evaporation of the acetone, the reaction mixture was diluted with water and then extracted with AcOEt. The extract was washed with brine, dried, and concentrated. The oily residue was chromatographed on silica gel with hexane–benzene (1 : 2) to give **16** (26 mg, 75%) as a colorless oil. IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 3075, 1740, 1640, 1005, 920. $^1$H-NMR (90 MHz, $CCl_4$) $\delta$: 0.82 (3H, s, 6-$CH_3$), 1.13 (3H, s, 6-$CH_3$), 4.7—5.1 (2H, m, $CH=CH_2$), 5.3—5.9 (1H, m, $CH=CH_2$). MS $m/z$ (%): 192 ($M^+$, 35), 82 (100). High MS Calcd for $C_{13}H_{20}O$: 192.1511. Found: 192.1483.

**6,6-Dimethyl-1-(2-oxopropyl)bicyclo[3.2.1]octan-8-one (17)**——A stream of oxygen was bubbled into a vigorously stirred mixture of **16** (32 mg, 0.17 mmol), CuCl (33 mg, 0.33 mmol), $PdCl_2$ (15 mg, 0.085 mmol), water (0.2 ml), and DMF (1.5 ml) at room temperature for 20 h. After dilution with water, the reaction mixture was acidified with concentrated HCl and extracted with ether. The extract was washed with saturated $NaHCO_3$ and brine, dried, and concentrated. The residue was chromatographed on silica gel with hexane–AcOEt (5 : 1) to give **17** (24 mg, 69%) as a colorless oil. IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 1745, 1720. $^1$H-NMR (90 MHz, $CCl_4$) $\delta$: 0.99 (3H, s, 6-$CH_3$), 1.18 (3H, s, 6-$CH_3$), 2.12 (3H, s, $COCH_3$), 2.58 (2H, s, 1-$CH_2$). MS $m/z$ (%): 208 ($M^+$, 100). High MS Calcd for $C_{13}H_{20}O_2$: 208.1463. Found: 208.1468.

**11,11-Dimethyltricyclo[4.3.2.0$^{1,5}$]undec-4-en-3-one (18)**——Potassium *tert*-butoxide (668 mg, 6.0 mmol) was added to a solution of **17** (124 mg, 0.60 mmol) in *tert*-BuOH (10 ml) and the mixture was stirred under reflux for 2 h. After cooling, the reaction mixture was neutralized with 1 N HCl and concentrated. The residue was taken up in AcOEt and the organic solution was washed with brine. The dried organic layer was concentrated to leave an oil, which was chromatographed on silica gel with hexane–AcOEt (6 : 1) to give **18** (92 mg, 81%) as a colorless oil. IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 1710, 1645. $^1$H-NMR (90 MHz, $CCl_4$) $\delta$: 0.90 (3H, s, 11-$CH_3$), 1.21 (3H, s, 11-$CH_3$), 1.33 (1H, d, $J$=13 Hz, 10-H), 1.78 (1H, d, $J$=13 Hz, 10-H), 2.20 (2H, s, 2-H), 2.41 (1H, br, 6-H), 5.67 (1H, s, 4-H). UV $\lambda_{max}^{EtOH}$ nm (log $\varepsilon$): 232 (4.18). MS $m/z$ (%): 190 ($M^+$, 28), 134 (100). High MS Calcd for $C_{13}H_{18}O$: 190.1358. Found: 190.1364.

**2-Methoxymethyl-11,11-dimethyltricyclo[4.3.2.0$^{1,5}$]undec-4-en-3-one (19)**——A solution of **18** (0.050 g, 0.26 mmol) in dry THF (3 ml) was added dropwise to a stirred solution of LDA [prepared from iso-$Pr_2NH$ (53 mg, 0.52 mmol) and 1.4 M *n*-BuLi (0.37 ml, 0.52 mmol)] in dry THF (3 ml) at −78 °C. Stirring was further continued for 10 min at this temperature. Chloromethyl methyl ether (63 mg, 0.78 mmol) was added to the mixture at −78 °C and the whole was stirred for 12 h. During this time, the reaction mixture was gradually warmed to room temperature. After addition of saturated aqueous $NH_4Cl$ solution, the mixture was extracted with ether. The extract was washed with brine, dried, and concentrated to leave an oil, which was chromatographed on silica gel with hexane–AcOEt (10 : 1) to give **19** (41 mg, 67%) as a colorless oil. IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 1705, 1645. $^1$H-NMR (90 MHz, $CCl_4$) $\delta$: 0.88 (3H, s, 11-$CH_3$), 1.22 (3H, s, 11-$CH_3$), 2.14 (1H, dd, $J$=9, 4 Hz, 2-H), 2.36 (1H, m, 6-H), 3.19 (3H, s, $CH_2OCH_3$), 3.28 (1H, dd, $J$=9.5, 9 Hz, $CH_2OCH_3$), 3.45 (1H, dd, $J$=9.5, 4 Hz, $CH_2OCH_3$), 5.55 (1H, s, 4-H). UV $\lambda_{max}^{EtOH}$ nm (log $\varepsilon$): 237(4.18). MS $m/z$ (%): 234 ($M^+$, 16), 105 (100). High MS Calcd for $C_{15}H_{22}O_2$: 234.1618. Found: 234.1603.

**(1*RS*,5*SR*)-2-Methoxymethyl-11,11-dimethyltricyclo[4.3.2.0$^{1,5}$]undecan-3-one (20)**——A solution of **19** (18.4 mg, 0.079 mmol) in MeOH (1 ml) was hydrogenated over 5% Pd–C (*ca.* 10 mg) under a pressure of 1 atm at room temperature for 12 h. The catalyst was filtered off and the filtrate was concentrated to leave an oil, which was chromatographed on silica gel with hexane–AcOEt (8 : 1) to give **20** (16.3 mg, 88%) as a colorless oil. IR $\nu_{max}^{CCl_4}$ cm$^{-1}$:

1740. $^1$H-NMR (90 MHz, $CCl_4$) $\delta$: 1.14 (3H, s, 11-$CH_3$), 1.16 (3H, s, 11-$CH_3$), 3.22 (3H, s, $CH_2OC\underline{H}_3$), 3.23 (1H, dd, $J$=10, 8.5 Hz, $C\underline{H}_2OCH_3$), 3.59 (1H, dd, $J$=10, 4.5 Hz, $C\underline{H}_2OCH_3$). MS $m/z$ (%): 236 ($M^+$, 20), 147 (100). High MS Calcd for $C_{15}H_{24}O_2$: 236.1773. Found: 236.1768.

**(1*RS*,5*SR*)-11,11-Dimethyl-2-methylenetricyclo[4.3.2.0$^{1,5}$]undecan-3-one [(±)-Descarboxyquadrone] (5)**——A mixture of **20** (15.9 mg, 0.067 mmol), TSA (trace), and dry benzene (1 ml) was heated at 45 °C for 5 h. After cooling, the reaction mixture was washed with saturated $NaHCO_3$ and brine, and dried. Evaporation of the solvent left an oil, which was chromatographed on silica gel with hexane–AcOEt (15 : 1) to afford (±)-**5** (13.3 mg, 97%) as a colorless semi-solid, mp < 30 °C. IR $\nu_{max}^{CCl_4}$ cm$^{-1}$: 1725, 1640. $^1$H-NMR (500 MHz, $CDCl_3$) $\delta$: 1.19 (3H, s, 11-$CH_3$), 1.23 (3H, s, 11-$CH_3$), 1.4—2.1 (10H, m), 2.48 (1H, dd, $J$=19.5, 9.2 Hz, 4-H), 2.67 (1H, dd, $J$=19.5, 12 Hz, 4-H), 5.08 (1H, d, $J$=1.2 Hz, C=$CH_2$), 5.88 (1H, d, $J$=1.2 Hz, C=$CH_2$). UV $\lambda_{max}^{EtOH}$ nm (log $\varepsilon$): 235 (3.84). MS $m/z$ (%): 204 ($M^+$, 92), 91 (100). High MS Calcd for $C_{14}H_{20}O$: 204.1515. Found: 204.1531.

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## References and Notes

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