

A Photochemical Route to 4-Alkyltropones including Nezukone

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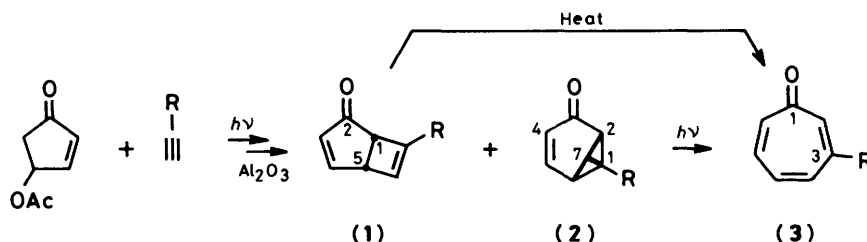
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An acetonitrile solution of acetylene and 3-methylcyclopent-2-enone (**4**) was irradiated with Pyrex-filtered light from a mercury lamp to give 5-methylbicyclo[3.2.0]hept-6-en-2-one (**6**) and 6-methyltricyclo[4.1.0.0^{2,7}]heptan-3-one (**8**). These were easily separated and when heated under reflux in Bu^tOH with SeO₂ gave the 4-methyltroponone valence-tautomer 5-methylbicyclo[3.2.0]hept-3,6-dien-2-one (**10**) and 4-methyltroponone (**12**), respectively, the latter in 20% overall, unoptimized yield. Similar reactions with 3-isopropylcyclopent-2-enone (**5**) in the place of (**4**) led to the natural troponoid 4-isopropyltroponone (nezukone) (**13**).

We have recently made more available the 3-alkyltropones (**3**) by light-induced cycloaddition of 4-acetoxycyclopent-2-enone to alkyl acetylenes followed by alumina treatment to give the intermediates (**1**) and (**2**) which were then transformed into the targets (**3**) by, respectively, pyrolysis or photoirradiation (Scheme 1).^{1,†}

Japanese nezuko tree or other plants of the same genus (*Thuja*), is a unique example of a natural 4-alkyltroponone,³ and has become a classical target in troponoid total synthesis.⁴ However, considering the relative simplicity of the nezukone structure, the synthesis so far described⁴ are lengthy and, with one exception,^{4a} require starting materials not readily available.



Scheme 1. Photo-induced synthesis of 3-alkyltropones

4-Alkyltropones, bearing no other substituent, are also rare compounds,² the best known of which is the antifungal 4-isopropyltroponone. This troponoid, isolated from either the

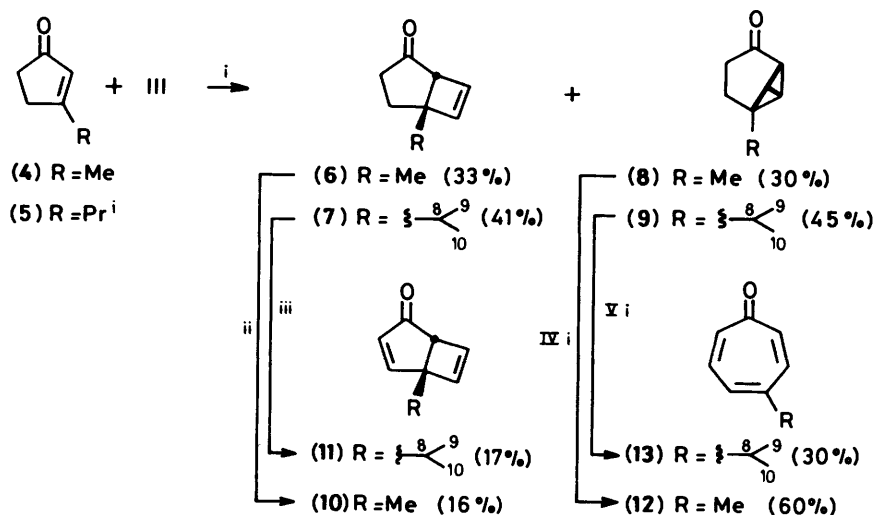
The literature in general, on 4-alkyl- (or aryl-) tropones, literature is very scanty.⁵

† Laser-light irradiation of a solution of 4-acetoxycyclopent-2-enone and hex-1-yne has now been repeated under previously described conditions.¹ Examination of the irradiated mixture by reverse-phase h.p.l.c. [Merck LiChrosorb RP8 column, 7 μ m, 25 \times 0.4 cm, MeCN-H₂O (1:1), 1 ml/min] has now revealed the formation of 6-butyl-*cis*-bicyclo[3.2.0]hepta-3,6-dien-2-one (8.1 min elution time) together with its 7-isomer (8.4 min), in a 3:7 ratio; this contrasts with our earlier report¹ to the effect that only the 7-isomer was formed. The 6-isomer has the following physical characteristics: it is an oil, λ_{max} (n-hexane) 350 nm (ϵ 64 l mol⁻¹ cm⁻¹); δ_{H} (CDCl₃; 300 MHz) 7.68 (dd, $J_{4,3}$ 5.7, $J_{4,5}$ 2.6, 4-H), 6.12 (ddd, $J_{3,4}$ 5.7, $J_{3,1}$ 1.0, $J_{3,5}$ 0.4, 3-H), 5.95 (dt, $J_{7,1}$ = $J_{7,1'}$ 1.2, 7-H), 3.78 (m, 5-H), 3.28 (m, 1-H), 2.10 (br t, $J_{1',2'}$ 7.0, 1'-H₂), 1.35 (m, 2'-H₂ and 3'-H₂), and 0.89 (t, $J_{4',3'}$ 7.0, 4'-H₃). On irradiation at δ 2.10 the δ 3.78 m became a dd, $J_{5,4}$ = $J_{5,1}$ 2.6 while the δ 3.28 m became a ddd, $J_{1,5}$ 2.6, $J_{1,7}$ 1.2, and $J_{1,3}$ 1.0; m/z 162 (11%, M^{++} - CH₃), 133 (20, M^{++} - C₂H₅ or HCO), 120 (19), 119 (62, M^{++} - C₃H₇), 105 (31, M^{++} - C₄H₉), 91 (100, 119 - CO), 77 (14), and 65 (14) (Found: C, 81.1; H, 8.8. C₁₁H₁₄O requires C, 81.4; H, 8.7%). During previous work¹ the 7-isomer was inadvertently obtained in pure form by cutting the central part of the preparative i.l.c. band. We have, in fact, now checked that previously reported n.m.r. data¹ refer to the pure 7-isomer. In view of these fresh results the formation of 1-butyltricyclo[4.1.0.0^{2,7}]hept-4-en-3-one on irradiation of a solution of 4-acetoxycyclopent-2-enone and hex-1-yne with a Hg-lamp¹ has to be attributed to an oxa-di- π -methane rearrangement of the an initially formed diastereoisomeric mixture of 4-acetoxy-6-butyl-*cis*-bicyclo[3.2.0]hept-6-en-2-one. Most likely this interpretation can also be extended to the hydroxypropyl analogues.¹

Synthesis.—We present here an extension of the method described above for 3-alkyltropones,¹ to the synthesis of 4-alkyltropones. Not only is the methodology more expeditious than that described earlier for compounds of this class,^{4,5} but also makes use of readily available starting materials.

First, we attempted to turn to our use the concepts of Scheme 1 by simply replacing alkylacetylenes with acetylene itself and 4-acetoxycyclopent-2-enone with analogous 3-alkyl derivatives. Unfortunately, the allylic bromination-acetoxylation route, while working satisfactorily with cyclopent-2-enone,⁶ proved not practicable with the 3-alkyl analogues, the two allylic positions competing for the brominating agent.⁶ Further, all attempts to proceed with dibrominated products proved frustrating.

In view of this, we turned our attention to the use either of commercially available 3-methylcyclopent-2-enone, or of the readily available (prepared photochemically) 3-isopropylcyclopent-2-enone,⁷ to be used within the concepts of Scheme 1. The hope was to introduce at a later stage the required enonic double bond into either the primary cycloadduct [(1)-type] or the product of the subsequent oxa-di- π -methane rearrangement⁸ [(2)-type]. Surprisingly, this proved difficult since, in our hands, efforts at trapping LDA-generated enolates of (**9**) with diphenyl disulphide^{9a,b} failed, while the α -brominated ketones PTAP-generated¹⁰ from (**7**) resisted all attempts at β -elimination.



Scheme 2. Photo-induced synthesis of 4-alkyltropones. *Reagents and conditions:* i, hv, MeCN, 0 °C, 10 h; ii, SeO₂, Bu^tOH, reflux, 2 h; iii, SeO₂, Bu^tOH, reflux, 3 h; iv, SeO₂, Bu^tOH, reflux, 1.5 h; v, SeO₂, Bu^tOH, 55 min

Finally, however, the problem was most expeditiously solved by using selenium dioxide (Scheme 2) to introduce the enonic double bond. While the bicyclic compounds (6) and (7) gave only poor yields of product in this reaction, the oxa-di- π -methane compound (8) gave the desired troponoid (12) in good yield. Although SeO₂ has already been used to introduce the enonic C=C double bond (without rearrangements),¹¹ the oxidation/rearrangement of (8) and (9) are remarkable. Thus, for the analogues (2), where the double bond was introduced by Al₂O₃-induced elimination of AcOH a long period of irradiation was required in order to induce isomerization to give troponoids.¹ For compound (9) the elimination-ring-opening with SeO₂ in Bu^tOH at reflux for 3 h gave nezukone (13) in only 4% yield; by shortening the reflux time to 55 min however the yield was raised to 30%. Since, under these conditions, all of (9) disappeared, it is likely, in view of the notorious instability of nezukone,³ that the yield can be increased by further shortening of the reflux time.

Structure Elucidation.—No comparison material was available to us and, further, since the ¹H n.m.r. data for (13) in the literature⁴ were obtained at lowfield there was no possibility of distinguishing between alkyltroponone isomers. In addition since there are no ¹H n.m.r. data in the literature for (12),⁵ we were faced with the problem of unambiguously establishing the structural identity of our products. To this end, we have run, and fully analyzed, both ¹H and ¹³C n.m.r. spectra at highfield for our products: these results should prove helpful for future structural assignments with these classes of compounds.

Key points in the assignment are as follows: the achiral tricyclic compounds (8) and (9) are distinguishable from their hypothetical, chiral isomers with the alkyl group at C-1, owing to the fact that with both (8) and (9) C-1 and C-7 are magnetically equivalent; correspondingly, 1-H and 7-H are magnetically equivalent, so that 2-H appears as a triplet. With both troponoids (12) and (13), the coupling patterns in the ¹H n.m.r. spectra (Experimental section) are only consistent with the spin mutual disposition of the 4-isomers (Experimental section), clearly ruling out the 2- or 3-isomeric structures.

Experimental

General Remarks.—Silica gel t.l.c. was carried out on Merck Kieselgel 60 PF₂₅₄ with, unless otherwise stated, light

petroleum-Et₂O (6:4). All evaporations were carried out at reduced pressure. Yields are based on reacted starting ketones. Photochemistry was carried out with a 125 W Pyrex-filtered, medium-pressure immersion Hg lamp, using a cylindrical reactor of 6.5 cm diameter, coaxial with the Hg lamp. U.v. and i.r. spectra are from a C. Erba Spectracomp-601 and Perkin-Elmer 337 and 983 spectrophotometers, respectively. ¹H N.m.r. spectra were recorded on either a Varian 360 (60 MHz) or a Varian XL300 spectrometer (300 MHz), while ¹³C n.m.r. spectra are from a Varian XL 300 spectrometer (75.429 MHz); δ values are given in p.p.m. with respect to internal SiMe₄ (0 p.p.m.) and coupling constants *J* are in Hz. Carbon multiplicities are from either off-resonance decoupling [compounds (8) and (11)] or the APT technique¹² [compounds (9), (12), and (13)]. Deuteriated Eu(fod)₃ (6,6,7,7,8,8,8-heptafluoro-2,2-di-[²H₃]methyl)[1,1,1-²H₃]octane-3,5-dionate was used in the lanthanide-induced-shift experiments. Mass spectra are from a home-built quadrupole, computerized spectrometer, based on the ELFS-4-162-8 Extranuclear quadrupole.

Photoreaction of 4-Methylcyclopent-2-enone (4) with Acetylene.—A solution of (4) (Aldrich) (2.5 g, 26 mmol) in MeCN (250 ml) was irradiated whilst acetylene was bubbled through it at 0 °C for 10 h; at this point there was a 37% conversion of (4). Evaporation of the mixture and preparative t.l.c. gave 5-methyl-cis-bicyclo[3.2.0]hept-6-en-2-one (6), *R_F* 0.67 (0.39 g, 3.20 mmol, 33%), 6-methyltricyclo[4.1.0.0^{2,7}]heptan-3-one (8), *R_F* 0.51 (0.35 g, 2.87 mmol, 30%), and unchanged (4), *R_F* 0.26 (1.57 g).

Compound (6) was an oil, ν_{max} (neat) 1 740 cm⁻¹; δ_{H} (CDCl₃, 60 MHz) 6.19 and 5.95 (two d, *J* 2.3 6-H and 7-H), 3.1–1.2 (series of m, 1-H, 3-H₂, and 4-H₂), and 1.05 (s, 8-H₃) (Found: C, 78.61; H, 8.31. C₈H₁₀O requires C, 78.65; H, 8.25%).

Compound (8) was an oil, ν_{max} (neat) 1 714 cm⁻¹; δ_{H} (CDCl₃, 300 MHz) 2.67 (t, *J*_{2,1} = *J*_{2,7} 3.0, 2-H), 2.19 (br d, *J* 3.0, 1-H and 7-H), 2.18 (t, *J*_{4,5} 7.3 4-H₂), 1.94 (br t, *J*_{5,4} 7.3, 5-H₂), and 1.22 (s, 8-H₃) (double irradiations revealed a long-range coupling, of too small magnitude to be evaluated, among the 1-H and 7-H, from one side, and 5-H₂, from the other side; δ_{C} (CDCl₃) 210.58 (s, C-3), 49.04 (d, C-2), 43.30 (s, C-6), 34.19 (t, C-4), 27.85 (t, C-5), 21.07 (q, C-8), and 14.76 (d, C-1 and C-7); *m/z* 122 (23%, *M*⁺), 107 (35, *M*⁺ - 15), 94 (16, *M*⁺ - 28), 79 (100, *M*⁺ - (15 + 28)), and 77 (27) (Found: C, 78.25; H, 8.27. C₈H₁₀O requires C, 78.65; H, 8.25%).

Photoreaction of 4-Isopropylcyclopent-2-enone (5) with Acetylene.—A solution of (5) (1.5 g, 12.1 mmol), prepared according to the literature,⁷ in MeCN (300 ml) was irradiated as with (4) above, whilst acetylene was bubbled through it for 10 h; there was a ca. 50% conversion of (5). T.l.c., as for (6)—(8), led to 5-isopropyl-cis-bicyclo[3.2.0]hept-6-en-2-one (7), R_F 0.70 (0.38 g, 2.5 mmol, 41%) and 6-isopropyltricyclo[4.1.0.0^{2,7}]hept-4-en-3-one (9) (0.41 g, 2.73 mmol, 45%), R_F 0.52, and unchanged (5), R_F 0.31 (0.75 g).

Compound (7) was an oil, ν_{\max} (neat) 1740 cm^{-1} ; δ_{H} (CDCl_3 , 60 MHz) 6.3 and 6.1 (two d, J 2.4, 6-H and 7-H), 2.9—1.3 (series of m, 1-H, 3-H₂, 4-H₂, and 8-H), 0.8 (d, J 6.5, 9-H₃ and 10-H₃) (Found: C, 79.85; H, 9.3. $\text{C}_{10}\text{H}_{14}\text{O}$ requires C, 79.95; H, 9.39).

Compound (9) was an oil, ν_{\max} (neat) 1715 cm^{-1} ; δ_{H} (CDCl_3 , 300 MHz) 2.65 (t, $J_{2,1} = J_{2,7}$ 2.9, 2-H), 2.17 (t, $J_{5,4}$ 7.3, 4-H₂), 2.16 (br d, J 2.9, 1-H and 7-H), 1.91 (br t, $J_{4,5}$ 7.3, 5-H₂), 1.58 (heptet, J 7.0, 8-H), and 0.97 (d, J 7.0, 9-H₃ and 10-H₃); δ_{C} (CDCl_3) 211.30 (s, C-3), 48.35 (d, C-2), 42.77 (s, C-6), 34.62 (t, C-4), 33.51 (d, C-8), 21.97 (t, C-5), 19.86 (q, C-9 and C-10), and 13.74 (d, C-1 and C-7) (Found: C, 79.95; H, 9.5. $\text{C}_{10}\text{H}_{14}\text{O}$ requires C, 79.95; H, 9.39); m/z 107 (100%, $M^{++} - 43$), 103 (3), 91 (44), 79 (84), and 77 (37).

Oxidation of Compound (6) with Selenium Dioxide.—A mixture of (6) (0.302 g, 2.47 mmol), SeO_2 (0.3 g), and Bu^tOH (9 ml) was refluxed, under N_2 , for 2 h. Evaporation and t.l.c. led to 5-methyl-cis-bicyclo[3.2.0]hepta-3,6-dien-2-one (10) (0.025 g, 0.2 mmol, 16%), R_F 0.47, and unchanged (6) (0.144 g).

Compound (10) was an oil, δ_{H} (C_6D_6 , 300 MHz) 6.67 (d, $J_{4,3}$ 5.8, 4-H), 6.03 (dd, $J_{7,6}$ 2.4, $J_{7,1}$ 1.3, A part of ABX, 7-H), 6.00 (d, $J_{6,7}$ 2.4, B part of ABX, 6-H), 5.71 (dd, $J_{3,4}$ 5.8, $J_{3,1}$ 1.5, 3-H), 2.79 (m, X part of ABX, 1-H), and 0.90 (s, 8-H₃) (Found: C, 79.95; H, 6.85. $\text{C}_8\text{H}_8\text{O}$ requires C, 80.00; H, 6.71); on double irradiation at δ_{H} 6.67, the 2.79 m became a doublet of doublets, J 1.3, 1.3.

Oxidation of Compound (7) with Selenium Dioxide.—A mixture of compound (7) (0.28 g, 1.87 mmol), SeO_2 (0.28 g), and Bu^tOH (10 ml) was refluxed, under N_2 , for 3 h. Evaporation and t.l.c. gave 5-isopropyl-cis-bicyclo[3.2.0]hepta-3,6-dien-2-one (11) (0.035 g, 0.236 mmol, 17%), R_F 0.56 and unchanged (7) (0.071 g).

Compound (11) was an oil, δ_{H} (C_6D_6 , 300 MHz) 6.80 (d, $J_{4,3}$ 5.9, 4-H), 6.11 (dd, $J_{7,6}$ 2.4, $J_{7,1}$ 1.5, A of ABX, 7-H), 6.09 (d, $J_{6,7}$ 2.4, B of ABX, 6-H), 5.78 (dd, $J_{3,4}$ 5.9, $J_{3,1}$ 2.0, 3-H), 2.95 (m, X of ABX, 1-H), 1.58 (heptet, J 6.8, 8-H), 0.64 and 0.59 (two, d, J 6.8, 9-H₃ and 10-H₃) (the δ_{H} 2.95 m became either a doublet of doublets, J 2.0, 1.5, or a doublet, J 1.5, on double irradiation at δ_{H} 6.80 or 5.78, respectively; δ_{C} (C_6D_6) 203.96 (s, C-2), 162.48 (d, C-4), 145.42 (d, C-3), 136.29 (d, C-7), 132.87 (d, C-6), 56.15 (d, C-1), 30.58 (d, C-8), 18.86 and 18.47 (two q, C-9 and C-10) (the C-5 resonance could not be easily detected); m/z 148 (0.9%, $M^{++} - 15$), 133 (64, $M^{++} - 15$), 119 (0.5), 105 (100, $M^{++} - 43$), 91 (16), 79 (23), and 77 (14) (Found: C, 81.05; H, 8.63. $\text{C}_{10}\text{H}_{12}\text{O}$ requires C, 81.04; H, 8.16%).

Oxidation-Rearrangement of Compound (8) with Selenium Dioxide.—A mixture of (8) (0.362 g, 2.97 mmol), SeO_2 (0.36 g), and Bu^tOH (9 ml) was refluxed, under N_2 , for 1.5 h after which time all of (8) had disappeared. Evaporation and t.l.c. led to

4-methyltropone⁵ (12) (0.218 g, 1.82 mmol, 61%), R_F 0.42 (with Et_2O).

Compound (12) was a colourless oil which slowly darkened to give tarry material even at -20°C , λ_{\max} (EtOH) 230 (log ϵ 4.40) and 315 nm (4.16); δ_{H} (C_6D_6 , 300 MHz) 6.88 (br d, $J_{2,3} = J_{7,6}$ 11.9, 2-H and 7-H), 6.26 (dd, $J_{6,7}$ 11.9, $J_{6,5}$ 8.8, 6-H), 6.16 (dd, $J_{3,2}$ 11.9, $J_{3,5}$ 1.7, 3-H), 5.96 (br d, $J_{5,6}$ 8.8, 5-H), and 1.55 (s, 8-H₃); δ_{C} (C_6D_6) 187.22 (s, C-1), 145.16 (s, C-4), 141.19 (d, C-7), 139.99 (d, C-2), 139.15 (d, C-6), 136.00 (d, C-3), 128.60 (d, C-5), and 25.76 (q, C-8); m/z 120 (16%, M^{++}), 92 (51, $M^{++} - \text{CO}$), 91 (100, $M^{++} - \text{HCO}$), and 77 (0.7).

Oxidation-Rearrangement of (9) with Selenium Dioxide.—A mixture of (9) (0.237 g, 1.57 mmol), SeO_2 (0.196 g), and Bu^tOH (5 ml) was refluxed, under N_2 , for 55 min, at which time (and perhaps even earlier, although not checked) all of (9) had disappeared. Evaporation and t.l.c. gave 4-isopropyltropone,^{3,4} (13) R_F 0.42 (with Et_2O) (0.07 g, 0.47 mmol, 30%).

Compound (13) was a colourless oil which tended to darken even in the cold, λ_{\max} . 230 (log ϵ 4.47) and 313 (4.17); ν_{\max} . 1 630, 1 559, 1 459, 1 235, and 866; δ_{H} (C_6D_6 , 300 MHz) 6.94 (ddd, $J_{2,3}$ 12.5, $J_{2,7}$ 3.3, $J_{2,5}$ 0.8, 2-H), 6.90 (ddd, $J_{7,6}$ 12.0, $J_{7,2}$ 3.3, $J_{7,5}$ 0.8, 7-H), 6.26 (dd, $J_{6,7}$ 12.0, $J_{6,5}$ 8.6, 6-H), 6.25 (dd, $J_{3,2}$ 12.5, $J_{3,5}$ 1.9, 3-H), 6.01 (dddd, $J_{5,6}$ 8.6, $J_{5,3}$ 1.9, $J_{5,7} = J_{5,2}$ 0.8, 5-H), 2.05 (heptet, J 7.2, 8-H), and 0.74 (d, J 7.2, 9-H₃ and 10-H₃); on addition of an equimolar (0.012 g) amount of Eu(fod)₃, the observed shifts were 2-H ($\Delta\delta$ 9.9), 7-H (9.6), 3-H (2.5), 6-H (2.9), 5-H (2.0), 8-H (1.4), and 9-Me and 10-Me (0.9); δ_{C} (C_6H_6) 186.93 (s, C-1), 154.49 (s, C-4), 142.14 (d, C-7), 140.34 (d, C-2), 136.46 (d, C-6), 135.61 (d, C-3), 129.21 (d, C-5), 37.62 (d, C-8), and 22.41 (q, C-9 and C-10); m/z 148 (12%, $M^{++} - \text{CO}$), 120 (2, $M^{++} - \text{CO}$), 105 (100, $M^{++} - 43$), 103 (6), 91 (5), 79 (13), 78 (2), and 77 (4).

Acknowledgements

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* Just to note how delicate the use of the APT technique¹² may be in certain instances, this signal was unrealistically obtained as 'up' using a typical¹² delay of 0.007 s. This anomaly may be attributed to an unusually large C-H coupling.¹³ The assignment of this resonance was made for comparison with compound (8), analysed by off-resonance decoupling.

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