Light-induced Synthesis of 3-Alkyltropones

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Irradiation of 4-acetoxycyclopent-2-en-1-one (1) and hex-1-yne (8) with Pyrex-filtered light of a Hg lamp, followed by AcOH elimination with alumina, gave 3-n-butyltropone (15), via intermediate 4-acetoxy-7-n-butyl-cis-bicyclo[3.2.0]hept-6-en-1-one (10) and 1-n-butyltricyclo[4.1.0.0²·⁷]hept-4-en-3-one (13) in 21% overall, unoptimized yield whereas when 350 and 363 nm laser light was used, only compound (10) was formed and was isolated as 7-n-butyl-cis-bicyclo[3.2.0]hepta-3,6-dien-1-one (11). 3-(2'-Hydroxyprop-2'-yl)tropone (16), similarly prepared from compound (1) and 2-methylbut-3-yn-2-ol (9), was dehydrated to give 3-isopropenyltropone (17), a synthetic precursor of β-dolabrin (18). 3-Methoxytropone (23) was similarly synthesized.

Though many synthetic routes to substituted tropones have been devised[1] and the specific problem of the synthesis of 2-alkyl-[2] and 2-aryl-tropones[2b] has been satisfactorily solved, 3-alkyltropones remain scarcely available. In fact, present methods require preformed tropones and are restricted to certain alkyl or alkenyl groups, such as in the stepwise transformation of the cycloadduct of 2-diazopropane with [4—7-η-(2-acetyl)tropone]tricarbonyliron into either 3-isopropyl- or 3-isopropenyl-tropone.[3] On the other hand, besides tropone and substituted tropones,[4] 3-alkyl- and 3-alkenyl-tropones in particular are either proven[3] or potential synthons for both natural and unnatural products.

In order to attempt to improve this situation, we have focussed our attention on the following facts. It is known that (Scheme 1) 4-acetoxycyclopent-2-en-1-one (1) undergoes a [2 + 2] photochemical cycloaddition with acetylene (2)* to give the diastereoisomeric mixture (3) which, in turn, gives compound (6) via an oxa-di-π-methane photorearrangement. Then, compound (6) eliminates AcOH on alumina to afford tropovalene (7).[6a] Also, unrelated work has shown that tropo-valene, prepared along other routes, undergoes a photorearrangement giving tropone (5).[7] Finally, it is also known that the acetate (3) gives the dienone (4) on alumina[6b] whilst compounds of type (4) can be pyrolysed to tropones.[8] According to the proposed mechanisms [an oxa-di-π-methane rearrangement[9] for the (3) —→ (6) change and a disrotatory electrocyclic ring opening for the (4) —→ (5) change,[8] Scheme 1] an alkyl substituent at either C-6 or C-1 in (3), or at C-7 in (4), would be carried over to C-3 in tropone (5), thus affording the desired 3-alkyltropone.

An appraisal of the literature showed that the cycloaddition of unsymmetrically substituted alkynes with either cyclopent-2-en-1-one[5d–f] or its 2-trimethylsilyl analogue[5f] either lacks selectivity[5f] or gives the C-6-alkylated isomer as a minor by-product.[5d,e] However, we are able to report here that, contrary to these unfavourable prospects, the photochemical route of Scheme 1 to 3-alkyltropones works satisfactorily.

Our initial experiments gave negative results, since on irradiation of compound (1) and excess of hex-1-yne (8) in MeCN with linearly polarized light (350 and 363 nm, jointly obtained from a laser source), the head-to-head cycloadduct (10) was formed in over 76% yield † whilst the C-6-isomer could not be detected at the level of ¹H n.m.r. sensitivity. This was confirmed by the examination of the mixture of Al₂O₃ treatment from which compound (11) was isolated. On prolonged irradiation, either in MeCN or in Me₂CO, the acetate (10) remained unaltered. Also, flash pyrolysis of the dienone (11) gave the desired tropone (15) in only 2% yield (Scheme 2).

However, changing to a medium-pressure, Pyrex-filtered Hg lamp,[5e,6a,c,d] under otherwise identical conditions to those used in the laser irradiation above, we obtained a mixture which was further irradiated in Me₂CO to give, after Al₂O₃ treatment (Scheme 2), the desired 1-butyltropovalene (13) in 25% yield overall, besides the bicycle (11) in 38% yield. Irradiation of compound (13) in Me₂CO led to 3-butyltropone (15) in 83% yield.‡§¶

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† It should be noted that the >76% yield of isolated (10) (Scheme 2) represents a lower limit due to deliberately non-exhaustive extractions and shortened work-up times devised so as to avoid AcOH elimination.

‡ The structures of both bicycloheptadienones (11) and (12) have been unambiguously assigned by ¹H n.m.r. spectra either in the presence of an added chemical-shift reagent or by double-resonance experiments. Data and interpretation are in the Experimental section.

§ Unless there is an (unlikely) directing effect of the AcO substituent in compound (1), the formation of the C-6-Buⁿ (and C-1-Buⁿ) isomers in the photoreaction of hex-1-yne with cyclopent-2-en-1-one carried out with a Hg lamp[5d,e] must be attributed to subsequent phototransformations of the primary head-to-head photoadduct. This is in fact transparent to our laser light whilst it absorbs the Hg lamp 303 and 313 nm emissions, which are not filtered by the Pyrex glass. Photosensitization by acetone, used as solvent [W. M. Horspool, in 'Photochemistry,' (Specialist Periodical Reports), The Chemical Society, London, 1979, vol. 10, p. 322], if it occurs at all, does not seem to be a stringent requisite for reactions of the type (3) —→ (6), since the alcohol (14) was obtained from irradiations in MeCN (Scheme 2). Selective formation of the head-to-head primary photoadduct (10) under laser irradiation recalls a formally similar phenomenon we have observed for enone–olefin [2 + 2] photocycloadditions and which proved to be synthetically quite useful (M. Zandomeneghi, M. Cavazza, L. Moi, and F. Pietra, *Tetrahedron Lett.*, 1980, 21, 213; W. Theilheimer, 'Synthetic Methods of Organic Chemistry,' Interscience, New York, 1980, vol. 34, p. XIV).

¶ All chiral compounds reported in this work are racemates. However, more could probably be learned about the mechanism of these photoreactions by producing these compounds in optically enriched form by the use of circularly polarized light[6b,10] in place of linearly polarized or non-polarized light. This would also afford, in parallel with what has already been obtained for species of type (11, 12),[6b,10] the chiroptical data for an interesting species such as (13).

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* [2 + 2] Photocycloadditions of alkynes with enones are well known[5] and have been extended to both oxa enones (P. Margaretha, *Chimia*, 1975, 29, 203) and p-quinones (S. P. Pappas and B. C. Pappas, *Tetrahedron Lett.*, 1967, 1597; S. P. Pappas, B. C. Pappas, and N. A. Portnoy, *J. Org. Chem.*, 1969, 34, 520). In the special case of compound (1) they are also known for either bis(trimethylsilyl)acetylene[6c] or dideuterioacetylene (in the latter case to obtain optically enriched (−)-[6,7-²H₂]bicyclo[3.2.0]hepta-3,6-dien-1-one in an asymmetric photosynthesis induced by left-circularly polarized light[6b]) as well as for other alkynes, which allowed the synthesis of both annelated tropovalenes[6d] and 4-acetoxytropovalene.[6e]
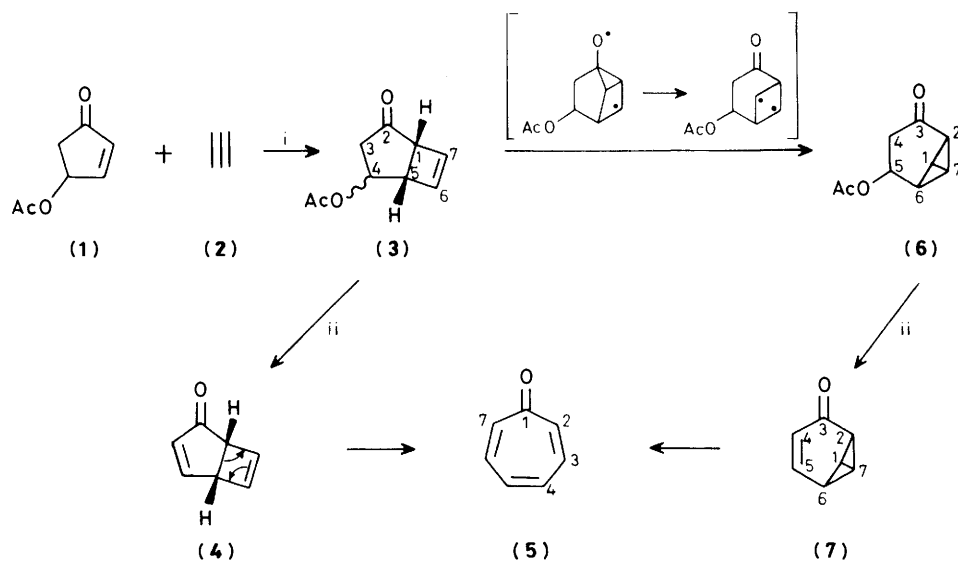
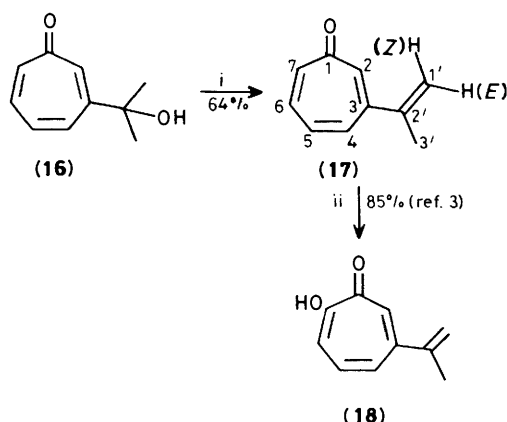Scheme 1. *Reagents and conditions:* i, *h*v; ii, Al$_2$O$_3$
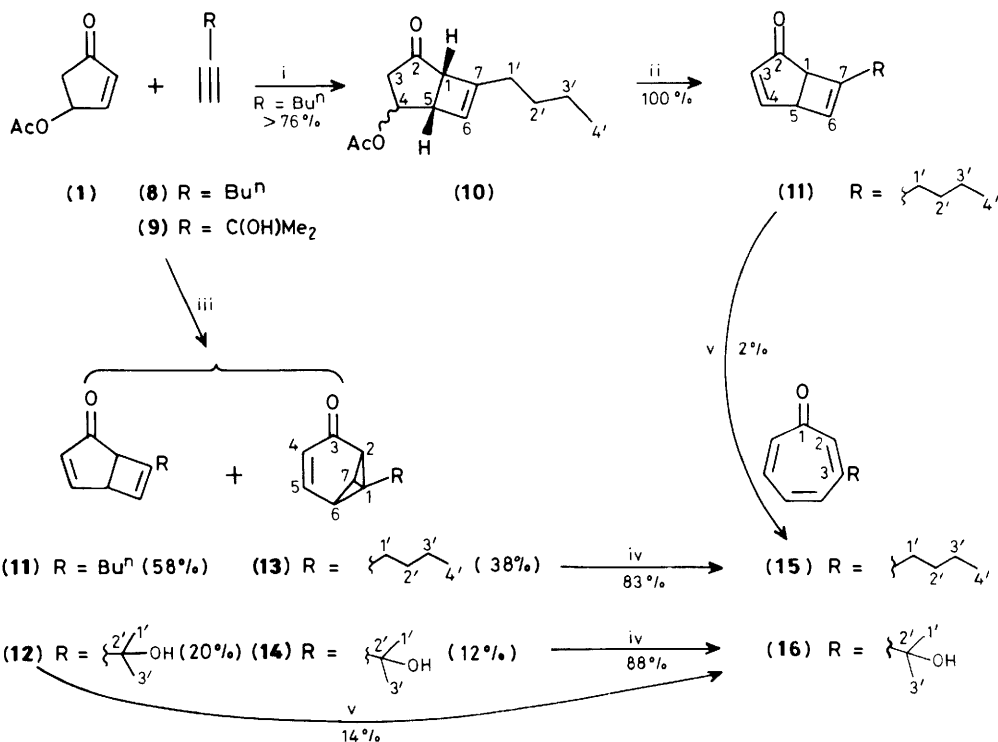
Scheme 2. *Reagents and conditions:* i, *h*v (laser); ii, Al$_2$O$_3$; iii, *h*v (Hg lamp); iv, *h*v (Hg lamp), acetone; v, heat

The use of 2-methylbut-3-yn-2-ol (9) in place of hex-1-yne (8) led to parallel results (Scheme 2) though the yields of isolated products from the photochemical reactions were lower as the hydroxylated products proved difficult to extract from either alumina or silica gel. However, flash pyrolysis of the alcohol (12) gave the 3-alkyltropone (16) in better yield than in the case of the n-butyl analogue (Scheme 2).

Conceivably, these yields could be improved by using longer irradiation times in order to generate more 7-alkyltropovalene.

Anyway, this method has the advantage of starting from easily accessible compounds and, moreover, it should not be overlooked that ring expansion of benzenoids, which is a classical entry to a variety of troponoids,[1a] failed for 3-isopropyltropone.[11]

As an application, we have carried out the dehydration of compound (16) with SOCl$_2$ to give 3-isopropenyltropone (17) in 64% isolated yield (Scheme 3). Since compound (17) has already been transformed into β-dolabrin (18),[3] we have thus

Scheme 3. *Reagents and conditions:* i, $SOCl_2$, pyridine; ii, N_2H_4, then KOH

accomplished a formal total synthesis of this natural tropolone from non-troponoidic compounds.*†

A limitation of the method of Scheme 2 lies in the fact that phenylacetylene failed to react with compound (1) in MeCN under our Hg lamp irradiation conditions. This is not surprising, however, when it is recalled that phenylacetylene showed aberrant photochemical behaviour with cyclopent-2-en-1-one.[5e,11]
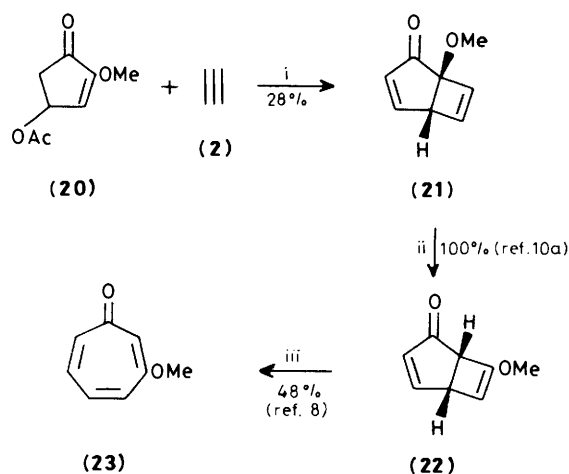
We have also looked for other routes to 3-alkyltropones, in particular trying to extend our method of substituting mobile groups on the tropone ring by lithium organocuprates; this worked pretty well for the synthesis of both 2-alkyl- and 2-aryl-tropones.[2b] However, this route has now proved uninteresting for the synthesis of 3-alkyltropones which have been obtained in extremely low yields [for example, Scheme 4, compound (15)]
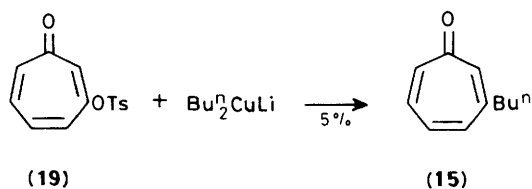
Scheme 4. *Solvent:* THF

in 5% yield] in addition to much tar, when lithium n-butyl-cuprate and the difficult-to-prepare[12] 3-tosyloxytropone (19) are used as starting materials.

Finally, we digress briefly to discuss alkoxytropones which are currently of interest (in particular 3-methoxytropones[13]) as synthons. Because of this, we have extended the photochemical method of Scheme 2 to the synthesis of 3-methoxytropone (23) by carrying out only the photocycloaddition of compound (20) with acetylene (2) to give 1-methoxy-*cis*-bicyclo[3.2.0]hepta-3,6-dien-1-one (21) (Scheme 5). The photoisomerization of

* Various other syntheses of β-dolabrin from either preformed troponoids (see ref. 3 and T. Nozoe, T. Mukai, and T. Asao, *Bull. Chem. Soc. Jpn.*, 1960, **33**, 1452) or from non-troponoids (D. Evans, D. J. Hart, and P. M. Koelsch, *J. Am. Chem. Soc.*, 1978, **100**, 4593; T. Asao, T. Machiguchi, T. Kitamura, and Y. Kitahara, *Chem. Commun.*, 1970, 89) have been carried out.
† It can also be envisaged that, in view of the known resistance of tropones to hydrogenation,[1a] 3-isopropyltropone could probably be easily obtained by catalytic hydrogenation of compound (17). Oxidation of 3-isopropyltropone could then offer an alternative[3] route to the natural tropolone β-thujaplicin.

Scheme 5. *Reagents and conditions:* i, *hv* (laser), then SiO_2; ii, *hv* (laser); iii, heat

compound (21) into (22) is known to proceed quantitatively under laser irradiation,[10a] whilst the vinylic ether (22) has been pyrolytically isomerized into tropone (23) in 48% yield.[8]‡

Experimental

General Remarks.—Silica gel t.l.c. was carried out on Merck Kieselgel 60 PF_{254}. C. Erba neutral Al_2O_3 was deactivated by 10% H_2O (w/w). All evaporations were carried out at reduced pressure. Laser photochemistry was carried out using linearly polarized light (the 350 and the 363 nm emission, jointly) from a Spectraphysics 171-19 Ar-ion, continuous-wave laser. The photochemical laser reactor for irradiations at 0 °C under N_2 (stirred solutions) under total absorption consisted of a cooled, 20 cm optical path cylindrical reactor of 2.0 cm internal diameter. For all other irradiations at 0 °C under N_2 (stirred solutions) we used Pyrex-filtered light from medium-pressure Hg lamps (80 W or 125 W, immersion, or 700 W, external, equipped with a parabolic reflecting mirror). A conventional, cylindrical, cooled reactor of 3.0 cm internal diameter was utilized for irradiations with an external Hg lamp. For immersion-lamp irradiations, a round reactor of 600 ml, coaxial with an internal Pyrex, water-cooled cylinder containing the Hg lamp was utilized. U.v. and i.r. spectra were recorded on Pye-Unicam SP8 150 and Perkin-Elmer 337 spectrophotometers. ^1H N.m.r. spectra were obtained with Varian 360 (60 MHz, having poor resolution) and Varian CFT20, modified for ^1H (80 MHz, set at 0.3 Hz resolution in the experiments reported here)

‡ In relation to this we note that 3-bromo-2-methoxycyclopent-2-en-1-one cannot be a substitute for the ynophile (20) since laser irradiation of this bromoenone in admixture with acetylene gave the debromo analogue which added to acetylene (2) to give the 3,4-dihydro analogue of compound (22). We were unable to transform the latter into the dienone (22) by selenium chemistry. Also, in a frustrating attempt to adapt these methods to the synthesis of 4-methoxytropones, we were unable to reproduce the stated (M. Kitamoto, S. Terashima, and S. Yamada, *Chem. Pharm. Bull.*, 1977, **25**, 41) good yields for the synthesis of 4-acetoxy-3-methoxycyclopent-2-en-1-one which we wanted to use as a starting compound for the irradiations. We have also found that bromination of 3-methoxycyclopent-2-en-1-one with *N*-bromo succinimide introduces first a bromine atom at C-2 and then a second one at C-4. 2,4-Dibromocyclopent-2-en-1-one was treated with silver acetate to give 4-acetoxy-2-bromo-3-methoxycyclopent-2-en-1-one which failed to react with excess of acetylene (2) under laser irradiation (350 and 363 nm, jointly, 0.6 W) for 2 h 20 min.

spectrometers; δ values are given in p.p.m. with respect to internal Me$_4$Si (0 p.p.m.) and coupling constants J are in Hz. Deuteriated Eu(fod)$_3$ {6,6,7,7,8,8,8-heptafluoro-2,2-di([^{2}H$_3$]-methyl)-[1,1,1-^{2}H$_3$]:octane-3,5-dionate} was used in lanthanide-induced-shift experiments. Mass spectra (e.i.) were obtained on a home-made computerized spectrometer built on a ELFS-4-162-8-Extranuclear quadrupole. Owing to the lack of both high-resolution mass measurements and of linked-scan experiments, the fragmentation attributions below are clearly tentative, though fully consistent with all other data.

Photochemical Synthesis of 3-*Butyltropone* (**15**).—(a) *Under laser irradiation.* A solution of compounds (**1**)^{6a} (0.43 g, 3.07 mmol) and (**8**) (8 ml, 70 mmol) in MeCN (50 ml) was irradiated at 0.5 W for 2 h. The solvent was evaporated off and the residue was purified by t.l.c. with Et$_2$O–n-hexane (6:4) as solvent to give the 4-*acetoxy-7-n-butyl-cis-bicyclo*[3.2.0]*hept-6-en-2-one* diastereoisomers (**10**) as a single spot, R_F 0.59 (0.325 g, 76%) and unchanged (**1**), R_F 0.35 (0.159 g). To a solution of this mixture (**10**) (0.325 g, 1.46 mmol) in a little Et$_2$O was added Al$_2$O$_3$ (3 g) and the mixture was kept at room temperature for 6 h. Et$_2$O extraction and evaporation led to pure 7-*n-butyl-cis-bicyclo*[3.2.0]*hepta-3,6-dien-2-one* (**11**) (0.23 g, 100%). The thermal isomerization of compound (**11**) into the tropone (**15**) is described below.

Data for *compound* (**10**): oil, $\lambda_{max.}$ (n-hexane) 302 nm (ε 30.4 l mol^{-1} cm^{-1}); δ$_H$ (CDCl$_3$; 60 MHz) 6.0 (m, 6-H), 5.2 (m, 4-H), 3.2 (m, 1- and 5-H), 2.0 (s, OAc, emerging from a br m for 1'-H$_2$ and 3-H$_2$), 1.3 (m, 2'- and 3'-H$_2$), and 0.9 (m, 4'-H$_3$), where the assignments were made by comparison with those for (**11**) below; m/z 162 (9%, $M^{+\bullet}$ − AcOH), further fragmentation being similar to that reported for (**11**) below (Found: C, 70.1; H, 8.3. C$_{13}$H$_{18}$O$_3$ requires C, 70.2; H, 8.2%).

Data for *compound* (**11**): oil, $\lambda_{max.}$ (n-hexane) 350 nm (70.0); δ$_H$ (CDCl$_3$; 80 MHz) 7.65 (dd, $J_{4,3}$ 5.7 and $J_{4,5}$ 2.6, 4-H), 6.15 (m, 6-H), 6.01 (ddd, $J_{3,4}$ 5.7, $J_{3,1}$ 0.9, and $J_{3,5}$ 0.3, 3-H), 3.74 (m, 5-H), 3.39 (m, 1-H), 2.12 (m, 1'-H$_2$), 1.38 (m, 2'- and 3'-H$_2$), and 0.87 (m, 4'-H$_3$). All these assignments rest on double-resonance experiments. In particular, on irradiation of the δ$_H$ 3.74 resonance the δ$_H$ 6.15 multiplet changed to doublets of a triplet, $J_{6,1'}$ 1.6, $J_{6,1}$ 0.3, whereas the δ$_H$ 6.01 resonance was observed as a doublet of doublets, with loss of the $J_{3,5}$ coupling, and, finally, the δ$_H$ 7.65 resonance was observed as a doublet, with loss of the $J_{4,5}$ coupling. However, the key irradiation was at δ$_H$ 2.12 whereby the δ$_H$ 3.74 resonance changed to doublets of doublets of a doublet with $J_{5,6} = J_{5,4} = 2.5$, $J_{5,1} = 0.6$, whereas the coupling constants given above for the δ$_H$ 6.01 resonance could be assigned and, most importantly, the δ$_H$ 3.39 resonance (1-H) was observed as a broad doublet, $J_{1,5}$ 2.5; should the butyl side-chain have been at C-6, a doublet of doublets would have been expected for 1-H instead. This was confirmed by the results of gradual addition of deuteriated Eu(fod)$_3$ whereby all signals shifted to lower field in the following decreasing order of chemical shifts 1-H > 3-H > 5-H > 1'-H$_2$ > 2'H$_2$ ≃ 6-H ≃ 4-H > 3'-H$_2$ > 4'-H$_3$, clearly indicating that the side-chain has to be at C-7 (under these conditions 1'-H$_2$ and 4'-H$_3$ were seen as triplets, $J_{1',2'}$ 5.9 and $J_{4',3'}$ 5.8, respectively); m/z 162 (6%, $M^{+\bullet}$), 147 (6, $M^{+\bullet}$ − CH$_3$), 133 (20, $M^{+\bullet}$ − CO), 119 (92, 147 − CO or $M^{+\bullet}$ − C$_3$H$_7$), 105 (21, 133 − CO or $M^{+\bullet}$ − C$_4$H$_9$), 91 (100, 119 − CO), 77 (18, 105 − CO), 65 (22), 51 (31), and 39 (27) (Found: C, 80.9; H, 8.8. C$_{11}$H$_{14}$O requires C, 81.4; H, 8.7%).

(b) *Under Hg lamp irradiation.* A solution of compounds (**1**) (1.17 g, 8.36 mmol) and (**8**) (40 ml) in MeCN (469 ml) was irradiated (80 W) for 5 h. A part (0.31 g) of the oily residue remaining after solvent evaporation was purified by t.l.c. as for method (a) above to give compound (**10**) (0.18 g, 65%). The other part (1.75 g) was dissolved in Me$_2$CO (450 ml) and

irradiated for 3 h at 80 W and for a further 3 h at 125 W. The solvent was evaporated off and the residue was worked up with Al$_2$O$_3$ (30 g) as for method (a) above to give an oil (1.1 g) which was purified by t.l.c. with Et$_2$O–n-hexane (1:1) as solvent to give compound (**11**), R_F 0.61 (0.48 g, 58%) and 1-*n-butyltricyclo*[4.1.0.0^{2,7}]*hept-4-en-3-one* (**13**), R_F 0.46 (0.32 g, 38%). A solution of this tricycle (**13**) (0.241 g, 1.49 mmol) in Me$_2$CO (60 ml) was irradiated (700 W) for 60 min. The solvent was evaporated off and the residue was purified by t.l.c. with n-hexane–THF (8:2) as solvent to give 3-*n-butyltropone* (**15**), R_F 0.23 (0.2 g, 83%).

Data for *compound* (**13**): oil, $\lambda_{max.}$(MeCN) 344 nm (37.0); $\nu_{max.}$(film) 1 680s cm^{-1}; δ$_H$ (CDCl$_3$; 80 MHz) 6.97 (dd, $J_{5,4}$ 9.8, $J_{5,6}$ 4.8, 5-H), 5.47 (br d, $J_{4,5}$ 9.8, 4-H), 3.21 (dd, $J_{7,6} = J_{7,2} =$ 2.1, 7-H), 2.60 (m, 2-H), 2.36 (partially submerged m, the centre of which was detected by double irradiation, 6-H), 2.04 (m, 1'-H$_2$), 1.36 (m, 2'- and 3'-H$_2$), and 0.92 (m, 4'-H$_3$). On gradual addition of deuteriated Eu(fod)$_3$ a general low-field shift of all resonances was observed in the following order of decreasing shift (where the shifts refer to 1.31 × 10^{-3} g of shift reagent added to ca. 0.7 ml of sample): 2-H (2.29 p.p.m.) > 4-H (2.22) ≫ 7-H (0.75) > 6-H (0.63) > 5-H (0.60) > 1'-H$_2$ (0.5) ≫ 4'-H$_3$ (0.1); under these conditions the 2-H multiplet became either a doublet of doublets, $J_{2,6}$ 4.3, $J_{2,7}$ 2.1, on irradiation at 4-H or a broad doublet of doublets, $J_{2,6}$ 4.4, $J_{2,4}$ 1.6, on irradiation at 7-H; in addition, the methyl group was clearly seen as a triplet, J 6.8; this coupling pattern agrees with that reported[7] for the parent compound (R = H); m/z 162 (5%, $M^{+\bullet}$), 147 (5), 133 (15), 119 (32), 105 (17), 91 (100), 77 (23), 65 (22), 51 (31), and 39 (27), i.e. the m.s. is quite similar to that reported above for (**11**), thus pointing to possible common gas-phase transformations (Found: C, 81.0; H, 8.9. C$_{11}$H$_{14}$O requires C, 81.4; H, 8.7%).

Data for *compound* (**15**): oil, $\lambda_{max.}$ (EtOH) 305 nm (6 000); $\nu_{max.}$(film) 1 622s and 1 580s cm^{-1}; δ$_H$ (CDCl$_3$; 60 MHz) 6.8 (m, troponoidic protons), 2.50 (t, J 7.6, 1'-H$_2$), 1.5 (m, 2'- and 3'-H$_2$), and 1.0 (m, 4'-H$_3$); m/z 162 (3%, $M^{+\bullet}$) and 91 (100) (Found: C, 80.8; H, 9.0. C$_{11}$H$_{14}$O requires C, 80.4; H, 8.7%).

Photochemical Synthesis of 3-(2'-*Hydroxypropan-2'-yl*)-*tropone* (**16**).—A solution of compound (**1**) (1.65 g, 18 mmol) and the alcohol (**9**) (50 ml) in MeCN (460 ml) was irradiated (80 W) for 8.5 h. The mixture was worked up as for method (b) above with Al$_2$O$_3$ (50 g) for 12 h and purified by t.l.c. with Et$_2$O as solvent to give 7-(2'-*hydroxypropan-2'-yl*)-*cis-bicyclo*[3.2.0]-*hepta-3,6-dien-2-one* (**12**), R_F 0.30 (0.40 g, 20%) and 1-(2'-*hydroxypropan-2'-yl*)*tricyclo*[4.1.0.0^{2,7}]*hept-4-en-3-one* (**14**), R_F 0.16 (0.23 g, 12%). A solution of the tricycle (**14**) (0.182 g, 1.11 mmol) in Me$_2$CO (60 ml) was irradiated (700 W) for 50 min. The solvent was evaporated off and the residue was purified by t.l.c. with Et$_2$O as solvent to give 3-(2'-*hydroxypropan-2'-yl*)*tropone* (**16**) (0.160 g, 88%).

Data for *compound* (**12**): oil, $\nu_{max.}$(film) 3 400s (OH) and 1 700 cm^{-1} (C=O); δ$_H$ (CDCl$_3$; 60 MHz) 7.6 (dd, J 5.7 and 2.6, 4-H), 6.2 (br s, 6-H), 6.0 (d, J 5.7, 3-H), 3.7 (m, 5-H), 3.5 (m, 1-H), 2.3 (br signal, OH), and 2.3 (s, 1'- and 3'-H$_3$); m/z 164 (3%, $M^{+\bullet}$), 149 (64, $M^{+\bullet}$ − CH$_3$), 146 (24, $M^{+\bullet}$ − H$_2$O), 131 (20, $M^{+\bullet}$ − CH$_3$ − H$_2$O), 121 (58, 121 − CO), 118 (32, 146 − CO), 103 (46, 131 − CO), 91 (61), 78 (95), 77 (72), and 43 (100) (Found: C, 73.0; H, 7.5. C$_{10}$H$_{12}$O$_2$ requires C, 73.1; H, 7.4%).

Data for *compound* (**14**): oil, $\nu_{max.}$(film) 3 480s and 1 680s cm^{-1} (C=O); δ$_H$ (CDCl$_3$; 60 MHz) 6.9 (dd, J 9.8 and 4.8, 5-H), 5.4 (br d, J 9.8, 4-H), 3.4 (m, 7-H), 2.7 (m, 2- and 6-H), and 1.2 (s, 1'- and 3'-H$_3$) (Found: C, 72.9; H, 7.6. C$_{10}$H$_{12}$O$_2$ requires C, 73.1; H, 7.4%).

Data for *compound* (**16**): oil, $\lambda_{max.}$ 303 nm (6 300); $\nu_{max.}$(film) 3 360s (OH), 1 635s (C=O), and 1 555s cm^{-1} (C=C); δ$_H$ (CDCl$_3$; 60 MHz) 7.4—6.8 (series of m, troponoidic protons), 3 (br signal, OH), and 1.5 (1'- and 3'-H$_3$); δ$_H$ (C$_6$D$_6$; 60 MHz) 7.7

(m), 7.1—6.1 (series of m, troponoidic protons), 4.6 (br signal, OH), and 1.5 (s, 1'- and 3'-H$_3$); m/z 164 (3%, $M^{+\cdot}$), 149 ($M^{+\cdot}$ − CH$_3$), 121 (149 − CO), 118 (17, $M^{+\cdot}$ − H$_2$O − CO), 103 (17), 91 (15), 78 (20), 77 (39), 59 (22), 50 (43), and 43 (100) (Found: C, 73.1; H, 7.5. C$_{10}$H$_{12}$O$_2$ requires C, 73.1; H, 7.4%).

Flash Pyrolyses.—(a) *Of compound* (12). With a similar apparatus to the one described previously,[8] compound (12) (0.155 g, 0.94 mmol) was pyrolysed at 390 °C. T.l.c. purification as for compound (16) above led to both the tropone (16) (0.016 g, 14%) and unreacted bicycle (12) (0.038 g).

(b) *Of compound* (11). This was carried out as described in (a), above either at 390 or 350 °C, to give the tropone (15) in 2% yield.

3-Isopropenyltropone (17).—To the alcohol (16) (0.035 g, 0.21 mmol) was added, at 0 °C, pyridine (0.2 ml) and SOCl$_2$ (0.04 ml) whereby a precipitate was formed. After 40 min the mixture was treated with CHCl$_3$, extracted with water, and the organic phase was dried over Na$_2$SO$_4$. Evaporation and t.l.c. of the residue with Et$_2$O as solvent gave the title tropone (17), R_F 0.44 (0.02 g, 64%); δ_H (CDCl$_3$; 60 MHz) as reported,[3] except that the δ_H 5.33, 5.28, and 2.10 resonances appear and must be described as multiplets; δ_H(C$_6$D$_6$) 7.1—5.8 (series of m, troponoidic protons), 4.92 [br s, 1'-H(E)], 4.80 [m, 1'-H(Z)], and 1.59 (m, 3'-H$_3$); m/z 146 (3%, $M^{+\cdot}$); 118 (91, $M^{+\cdot}$ − CO), 117 (100), 115 (31), 103 (71, $M^{+\cdot}$ − CO − CH$_3$), 91 (31), 84 (54), 78 (35), 77 (50), and 51 (34) (Found: C, 82.0; H, 7.0. C$_{10}$H$_{10}$O requires C, 82.2; H, 6.9%).

3-n-Butyltropone (15) *via the Cuprate Route.*—To lithium n-butylcuprate (2.0 mmol), prepared in THF (50 ml) at −78 °C as already described,[2b] was added, under N$_2$, the tosylate (19) (0.71 mmol). After 30 min the temperature was raised to room temp. and the mixture was neutralized with 5M HCl and extracted with Et$_2$O. The organic layer was washed with water, dried, evaporated, and the residue was purified by t.l.c. with benzene–95% EtOH (9.75:0.25) as solvent to give the tropone (15), R_F 0.35 (5%). U.v., ^{1}H n.m.r., and m.s. data are in accord with those reported above for compound (15).

Photochemical Synthesis of Compound (21).—A mixture made of 2-methoxycyclopent-2-en-1-one[14] (1.5 g, 13.4 mmol), an equimolar amount of NBS, and α,α'-azodi-isobutyronitrile (0.04 g) in CCl$_4$ (30 ml) was refluxed for 1.5 h. The mixture was cooled to room temp., filtered, and the solution was washed with water, dried and evaporated. The oily residue was dissolved in AcOH (15 ml), AcOAg (1.75 g) was added, and the mixture was refluxed for 8 h. Filtration, evaporation, and t.l.c. of the residue with Et$_2$O–n-hexane (8:2) as solvent led to two products. The minor product was the acetate (20), R_F 0.35 (0.20 g, 9%) (Found: C, 56.1; H, 6.0. C$_8$H$_{10}$O$_4$ requires C, 56.5; H, 5.9); $\lambda_{max.}$(MeCN) 314 nm (56); δ_H (CDCl$_3$; 60 MHz) 6.3 (d, J 3.4, 3-H), 5.7 (m, C part of ABC pattern, 4-H), 3.8 (s, OMe), 2.5 (m, AB part of ABC pattern, 5-H$_2$), and 2.0 (s, OAc). [The main product, R_F 0.67 (0.33 g), was not examined.] A solution of the acetate (20) (0.194 g, 1.15 mmol) in MeCN (40 ml) saturated at 0 °C with acetylene was laser-irradiated, as in the case of compound (1) above, at 0.7 W for 140 min. The solution was evaporated to dryness and the residue was purified by t.l.c. with

Et$_2$O–n-hexane (9:1) as solvent to give the bicycle (21),[10] R_F 0.52 (0.040 g, 28%), as well as unchanged acetate (20), R_F 0.43 (0.015 g).

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