Competition among 1,2- and 1,3-Acyl Shifts, and Reduction Reactions, in the UV Irradiation of Cyclopent-2-enones bearing a C-3 Terminal-alkyne Chain

Ines Mancini,[a] Marino Cavazza,[b] Graziano Guella[a] and Francesco Pietra[a]
[a] *Istituto di Chimica, Università di Trento, 38050 Povo-Trento, Italy*
[b] *Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via Risorgimento 35, 56100 Pisa, Italy*

UV irradiation in MeCN of 3-(pent-4'-ynyl)cyclopent-2-enone **13** (prepared from 3-iodocyclopent-2-enone **12** and the cuprate obtained from 5-iodopent-1-yne **10a**) gave mainly the hydrogen-addition product of the primary photocycloadduct **15**, tricyclo[5.3.0.0^{3,7}]decan-4-one **18a** (56%), besides minor **16** (22%), **19** (12%), **17** (8%) and traces of **15** (2%). In acetone as solvent, formation of **18a** remained the main route owing, presumably, to strain release on hydrogen addition in the primary photocycloadduct **15**. In CD_3CN as solvent, photoconversion of **13** was slower, deuterium was incorporated at the tertiary bridgeheads in the reduction product **18b**, and the product balance was slightly in favour of the 1,2-acyl-shift product **16**. This situation was not substantially ameliorated even in the typically reduction-hindering solvent hexadeuterioacetone. UV irradiation of the side-chain homologous 3-(hex-5'-ynyl)cyclopent-2-enone **14** in MeCN led to mainly the products of [2 + 2] photocycloaddition (tricyclo[5.4.0.0^{3,7}]undec-10-en-7-one **20**) and 1,3-acyl-shift (tricyclo[4.3.2.0^{1,6}]undec-10-en-7-one **21**), albeit in modest yields, 12 and 24%, respectively.

We have recently exploited the oxa-di-π-methane rearrangement (1,3-acyl shift)[1] of the cycloadducts obtained from irradiation of 4-acetoxycyclopent-2-enone **1a** and monoalkylacetylenes **2a**, or of 3-alkylcyclopent-2-enones **1b** and acetylene **2b**, for the synthesis of the otherwise difficult to obtain 3-alkyltropones **5**[2a] or 4-alkyltropones **8**[2b] (Scheme 1). A variant of this methodology has furnished the simplest and most efficient entry to the rare γ-tropolone.[2c]

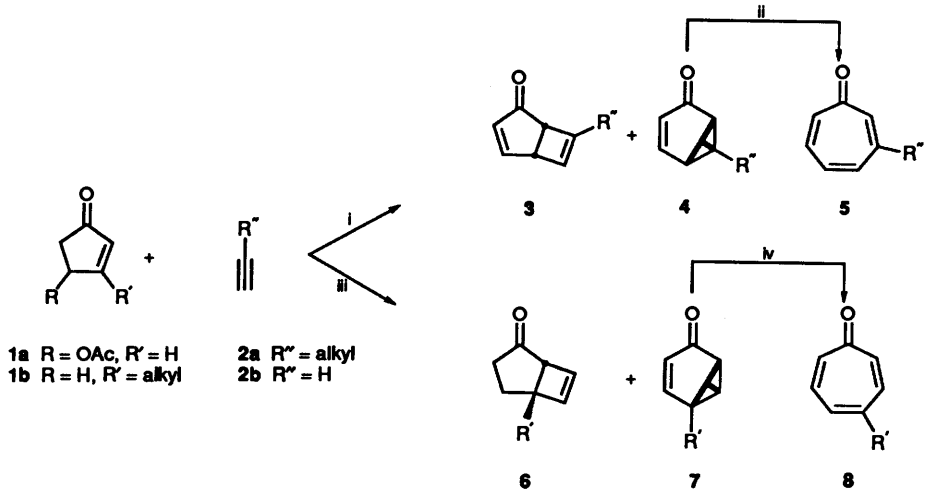
We wondered whether an intramolecular version of these methodologies was possible; this is, in fact, a rather underdeveloped area. We know, albeit in a different context, of one example of intramolecular photochemical cycloaddition of a terminal alkyne to a cyclopent-2-enone unit,[3a] and of other examples of photocycloaddition of terminal alkynes,[3b,c] or disubstituted alkynes[3d] to a cyclohex-2-enone unit.[3b-d] We report here that on UV irradiation of cyclopent-2-enones bearing a terminal-alkyne C-5 chain, the oxa-di-π-methane rearrangement was only observed as a minor pathway. The initial [2 + 2] photocycloadduct was mainly diverted along hydrogen addition of 1,3-acyl shift pathways, depending on the length of the alkyne side-chain.

Results and Discussion

We observed previously that, on irradiation of 4-acetoxycyclopent-2-enone **1a** with alk-1-ynes **2a** in MeCN with Pyrex-filtered light from a medium-pressure Hg lamp, the head-to-tail initial photocycloadduct undergoes oxa-di-π-methane rearrangement to give a product of type **4**, whereas the head-to-head type cycloadduct **3** is recovered unchanged (Scheme 1).[2a] The acyl group in **1a** served to carry into the primary photocycloadduct a masked C=C bond, to be then set free by Al_2O_3 treatment giving products **3** and **4**.

Unpublished data from our laboratories have confirmed that the cycloaddition of cyclopent-2-enone with *sym*-disubstituted alkynes (hex-3-yne) gives products of both [2 + 2] cycloaddition and a 1,3-acyl shift.[4] It is clear from these examples that γ-alkylated cycloadducts resist the oxa-di-π-methane photorearrangement, being prone to 1,3-acyl shift instead. Therefore, light-induced 1,3-acyl shifts may have passed unnoticed in previous examples of UV irradiation of cyclopent-2-enones with alk-1-ynes[2] (Scheme 1) because the primary [2 + 2] photocycloadduct itself was regenerated in the process.

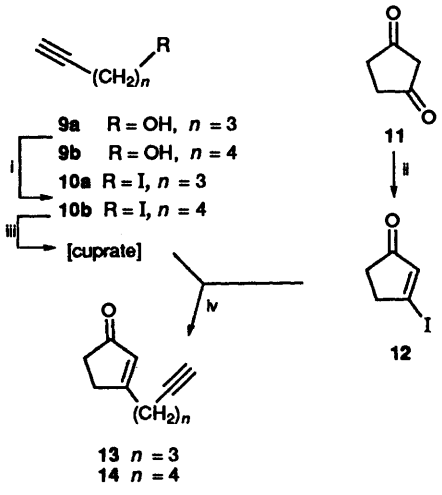
We were thus prompted to examine the photochemical



Scheme 1 Photoinduced synthesis of 3- or 4-alkyltropones.[2a,b] *Substituents and reagents:* i, R = OAc, R' = H, R'' = alkyl, *hv* followed by Al_2O_3; ii, *hv*; iii, R = R'' = H, R' = alkyl, *hv*; iv, SeO_2.

behaviour of cyclopent-2-enones with a C-3 side-chain bearing an unsubstituted alkyne terminus. This leaves the γ-position unsubstituted in the primary [2 + 2] photocycloadduct, thus potentially opening the route to 1,2-acyl shifts.

Compounds **13** and **14** were needed to check the above point. However, what was thought to be an obvious sequence to obtain these compounds *via* addition, in THF, to 3-ethoxycyclopent-2-enone of the Grignard reagents obtained from either 5-bromo-1-trimethylsilylpent-1-yne or 6-bromo-1-trimethylsilylhex-1-yne, followed by hydrolysis and then removal of the Me_3Si group, actually resulted in low yields (30–40%) owing to enolization problems.[3c] At reflux, only the product of intramolecular cyclization of the Grignard reagents obtained from 6-bromo-1-trimethylsilylhex-1-yne, *via* intramolecular carbometallation, was obtained.[5] This undesired process was previously observed also with the corresponding organolithium reagent.[3c] Luckily, organocopper reagents[6] solved our problem satisfactorily (Scheme 2) leading from **10a** or **10b** (obtained from **9a** or **9b**)[7] and **12** (obtained from **11**)[8] to **13** or **14** in overall 85% yield without the need to protect the terminal acetylene group.



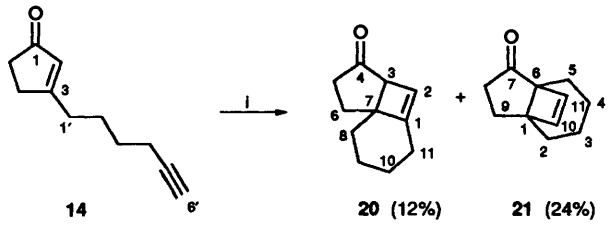
Scheme 2 Synthesis of **13** and **14**. *Reagents and conditions:* i, Ph_3P, I_2, imidazole, CH_2Cl_2, room temp., 3 h, 88%; ii, Ph_3P, I_2, Et_3N, reflux, 4 h, 87%; iii, activated Zn, THF, 30 °C, CuCN·2LiCl, −20 °C; iv, cooling to −60 °C, addition of **12**, then −10 °C overnight, 85%.

UV irradiation of compound **13** proved to be complex, however. Mainly the product **18a** of hydrogen addition to the initial [2 + 2] photocycloadduct **15** was obtained, accompanied by those of 1,2- **16*** and 1,3-acyl shifts **17**, and of reduction of the latter to **19** (Scheme 3). In acetone as solvent, reduction to **18a** remained the main route owing, presumably, to strain release on hydrogen addition in the primary photocycloadduct **15**.

Interestingly, in CD_3CN as solvent, photoconversion of **13** was slower, deuterium being incorporated at the tertiary bridgeheads of **18b**, whereas the product balance was slightly in favour of the 1,2-acyl-shift product **16** (Scheme 3).† Hexadeuterioacetone as solvent failed to further favour the 1,2-acyl shift product, and reduction products of type **18** still dominated.

That **18b** carries deuterium at C-1 and C-3 was proven by the absence of (a) ^1H NMR and ^1H–^1H COSY signals for 1-H and 3-H and (b) long-range couplings with 5-H (which, in contrast, were clearly observed in compound **18a**, Experimental section). Deuterium incorporation at C-1 and C-3 in **18b**, in a process involving a primary kinetic isotope effect, suggest the intervention of radical species that abstract hydrogen from the solvent. This implies that photoreduction of strained β,γ-enones, already observed for the phototransformation of **17** into **19**[12a] and **18a**,[12b] must follow complex routes that warrant mechanistic investigation.

Compound **14**, which bears a longer side-chain, gave mainly the initial [2 + 2] photocycloadduct, **20**,‡ and that of 1,3-acyl shift, **21** (Scheme 4).



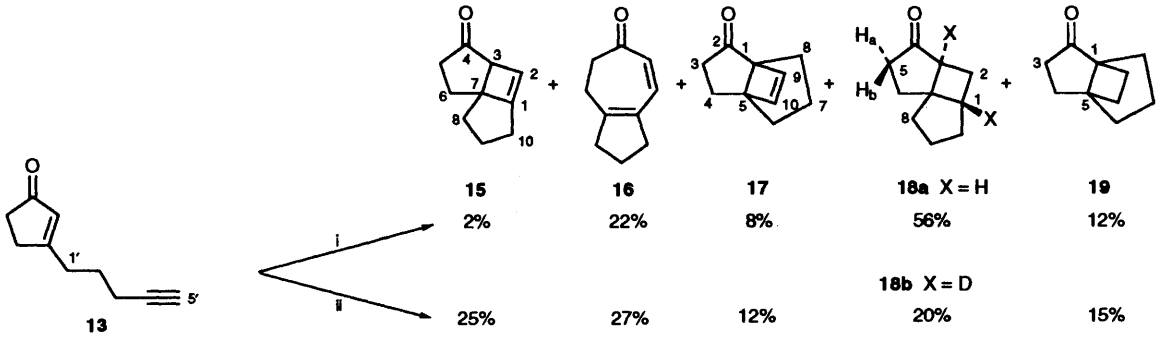
Scheme 4 UV irradiation of **14** with immersion lamp. *Reagents and conditions:* i, *hv*, MeCN.

It can be assumed that compound **18a** derives from the primary cycloadduct **15** *via* H-abstraction from the solvent by a free-radical intermediate, in contrast with the behaviour of compound **20**, which gives mainly **21** *via* a 1,3-acyl shift. This can be explained on the basis of strain release on hydrogen

* During the NMR study in $CDCl_3$, **16** underwent partial degradation to give unidentified products of higher polarity.

† The structures of the above and following compounds are supported by analytical and spectral data in the Experimental section, in comparison with literature data.[9,11] Because of the high volatility of these compounds, the yields given in this work represent a lower limit.

‡ The tricyclic enone **20** was previously obtained *via* base-induced rearrangement–elimination of a chlorine-bearing carbinol.[13]



Scheme 3[a,b] UV irradiation of **13** with immersion lamp (external-lamp irradiation gave similar results). [a] Numbering of **18a** and **19** is for convenience. [b] Yields, evaluated by integration from ^1H NMR spectra of the irradiated mixtures, are given with respect to reacted enone **13** (i: 41%, ii: 50%). *Reagents and conditions:* i, *hv*, MeCN; ii, *hv*, CD_3CN.

addition at the tertiary bridgeheads of **15**. In related cases, the presence of a methyl substituent offered an intramolecular H-shift pathway for energy release. Thus, UV irradiation of the 9,10-dimethyl analogue of **17** gave the 2-*exo*-methylene-3-methyl analogue of **15** *via* a 1,3-acyl shift followed by an allylic-proton shift.[14] Lacking excess strain energy, the 10,11-dimethyl analogue of **21**, on UV irradiation at low conversion gave the normal product of 1,3-acyl shift, *i.e.*, the 2,3-dimethyl analogue of **20**.[14]

In conclusion, although failing to provide efficient new oxa-di-π-methane rearrangements, which could have opened new routes to annulated troponoids,* these studies revealed interesting facets of the photochemistry of the α,β-enone-alkyne systems. The main point is that, contrary to the norm, where acetone as solvent acts as a triplet sensitizer, favouring the 1,2- *vs.* the 1,3-acyl shift,[1] in our multistep processes acetone merely acts as a light filter, reducing the number of photons available to the reacting system. Because of this, the ratio of yields for products of [2 + 2] cycloaddition over those of 1,3-acyl shift was larger in acetone than in acetonitrile. This suggests that both the 1,2- and the 1,3-acyl shifts observed here follow direct light absorption. For the 1,2-shifts, this conclusion is also implied by the following observations.[2a] Irradiation of 4-acetoxycyclopent-2-enone and hex-1-yne in MeCN with linearly polarized light (350 and 363 nm, jointly) from a laser source induced only [2 + 2] cycloaddition, while no rearrangement was observed.[2a] Replacing the laser with a Pyrex-filtered medium-pressure Hg lamp led to products of oxa-di-π-methane rearrangement of the initial [2 + 2] photoadduct. Therefore, this rearrangement must be imputed to the directly absorbed 313, 303 and 297 nm Hg emissions.[2a]

Experimental

General.—All evaporations were carried out at reduced pressure at room temperature. Yields are based on material which reacted. Flash chromatography (FC) was performed on Merck Si-60, 15–25 μm; TLC on Merck Kieselgel 60 F_{254} plates; HPLC on a Merck LiChrosorb Si-60 (7 μm) 25 × 1 cm column; and reversed-phase HPLC on Spherisorb RP-18 (7 μm) 250 × 4.6 mm column (with UV monitoring at λ 220 nm, unless otherwise stated, and solvent flux 5 cm^3 min^{-1}). NMR spectra were obtained in $CDCl_3$ using a Varian XL-300 spectrometer (^1H 299.94, ^{13}C 75.43 MHz) or a Varian Gemini BB200 spectrometer (^1H 199.975 MHz) only for the hexadeuterioacetone experiment; δ values are reported with respect to internal $SiMe_4$ (δ 0) and *J* values in Hz; multiplicities from DEPT.[17] The assignments were confirmed by ^1H–^1H[18] and ^1H–^{13}C COSY.[19] EIMS spectra were taken using a Kratos MS80 mass spectrometer with home-built acquisition system.

Materials.—Et_3N was distilled from BaO just before use, and THF or CH_2Cl_2 over $LiAlH_4$ or CaH_2, respectively, and stored over flame-dried 4 Å molecular sieves. LiCl was dried *in vacuo* at 140 °C for 1 h. All thermal reactions were carried out in flame-dried glassware under N_2, unless otherwise stated. HPLC-grade MeCN Carlo Erba RS, Me_2CO Merck Pro Analysi, 99.95% CD_3CN Merck for NMR spectroscopy and 99.5% CD_3COCD_3 Carlo Erba were used as such for the UV irradiations.

Photochemical Methodology.—Irradiations were carried out with a water-cooled, Pyrex-filtered 125 W medium-pressure Hg lamp. The lamp was either (a) immersed in the solution of the reagents in a 150 cm^3 cylindrical reactor, or (b) placed externally at 5 cm from a 10 cm^3 tube of 1.5 cm diameter containing the solution of the reagent, and the whole system being surrounded by reflecting aluminium foil. The solutions were degassed with Ar by freeze–thawing before irradiation. Reaction progress was monitored by reversed-phase HPLC with MeCN–H_2O (75:25), λ 254 nm, following the enone disappearance. The irradiated mixture was evaporated and the residue subjected to either flash chromatography (FC) or preparative TLC with light petroleum–Et_2O (3:2).

Preparation of 3-(*Pent-4-ynyl*)*cyclopent-2-enone* **13** *and* 3-(*Hex-5′-ynyl*)*cyclopent-2-enone* **14**.—To a stirred solution of Ph_3P (3.93 g, 15 mmol) in CH_2Cl_2 (45 cm^3) were added, in rapid succession, imidazole (1.02 g) and I_2 (3.80 g) in equimolar amounts followed, after 30 min, by a solution of **9a** (Aldrich) (1.2 cm^3, 12.9 mmol) in CH_2Cl_2 (15 cm^3). The mixture was stirred for 3 h, after which it was evaporated, and the residue subjected to FC with hexane to give **10a**; this was finally purified by distillation (b.p. 82 °C/40 mmHg) (2.20 g, 88%). By a similar procedure, **9b** (Aldrich) gave **10b**, which was used as eluted from FC (2.46 g, 91%). In a two-necked flask, Zn dust (1.53 g, 23.4 mmol) was flushed with Ar and then THF (2 cm^3) and 1,2-dibromoethane (0.1 cm^3) were added to it. The mixture was stirred at 60 °C for a few minutes after which it was cooled to room temperature and treated with TMSCl (0.1 cm^3); further stirring for 15 min gave activated Zn dust. To this was added dropwise a solution of **10a** (2.08 g, 10.7 mmol) in THF (3 cm^3) with stirring at 30 °C. Stirring was continued for 1.5 h after which it was stopped and Zn in excess was allowed to settle during 1 h. The supernatant was transferred by a syringe to another two-necked flask containing a solution of CuCN (0.75 g, 8.4 mmol) and LiCl (0.70 g, 16.8 mmol) in THF (5 cm^3) cooled to −20 °C under Ar, to give immediate formation of a deep-red suspension of the copper reagent. The mixture was cooled to −60 °C, and treated with a solution of **12**[8] (0.76 g, 3.67 mmol) in THF (3 cm^3); it was then stirred at −30 °C for 1 h and at −10 °C overnight. After this it was diluted with water (3 cm^3) and aq. NH_4Cl (2 cm^3) and paper filtered. The filtrate was concentrated and the aqueous layer was extracted with Et_2O (3 × 10 cm^3); the organic layer was dried (Na_2SO_4) and evaporated to give a crude oil that was subjected to FC with hexane–EtOAc gradient elution to give pure **13** (0.46 g, 85%). Following a similar procedure **10b** gave **14** (83%).

Compound **10a**. Colourless oil; δ_C 5.05 (t, C-1), 19.38 (t, C-3), 31.73 (t, C-2), 69.41 (d, C-5) and 82.18 (s, C-4); δ_H 1.97 (t, $J_{5,3}$ 2.7, 5-H), 1.98 (quint, $J_{2,1} = J_{2,3}$ 6.9, 2-H_2), 2.31 (td, $J_{3,2}$ 6.9, $J_{3,5}$ 2.7, 3-H_2) and 3.28 (t, $J_{1,2}$ 6.9, 1-H_2); *m/z* 194 ($M^{\bullet+}$, 36%), 155 (6) and 67 (100).

Compound **10b**. Colourless oil; δ_C 6.07 (t, C-1), 17.24 (t, C-4), 28.90 and 32.05 (2 t, C-3 and -2), 68.85 (d, C-6) and 83.46 (s, C-5); δ_H 1.59 and 1.90 (2 quint, $J_{3,4} = J_{3,2} = J_{2,1}$ 6.9, 3- and 2-H_2), 1.94 (t, $J_{6,4}$ 2.7, 6-H), 2.18 (td, $J_{4,3}$ 6.9, $J_{4,6}$ 2.7, 4-H_2) and 3.16 (t, $J_{1,2}$ 6.9, 1-H_2); *m/z* 208 ($M^{\bullet+}$, 2%) and 81 (36).

Compound **13**. Pale-yellow oil (Found: C, 81.2; H, 8.3. $C_{10}H_{12}O$ requires C, 81.04; H, 8.16%); ν_{max}(neat)/cm^{-1} 3280, 2940, 2130 (HC≡C), 1725 (C=O), 1620 (C=C) and 1430; δ_C 18.08 (t, C-3′), 25.71 (t, C-2′), 31.51 (t, C-4), 32.25 (t, C-1′), 35.24 (t, C-5), 69.29 (d, C-5′), 83.15 (s, C-4′), 129.72 (d, C-2), 181.63 (s, C-3) and 209.88 (s, C-1); δ_H 1.80 (quint, $J_{2',1'} = J_{2',3'}$ 6.9, 2′-H_2), 1.98 (t, $J_{5',3'}$ 2.7, 5′-H), 2.26 (td, $J_{3',2'}$ 6.9, $J_{3',5'}$ 2.7, 3′-H_2), 2.40 (m, 5-H_2), 2.53 (t, $J_{1',2'}$ 6.9, 1′-H_2), 2.57 (m, 4-H_2) and 5.96 (br quint, *J* 1.5, 2-H); *m/z* 148 ($M^{\bullet+}$, 15%), 120 (24), 119 (50), 105 (42), 91 (100), 81 (35), 67 (26) and 53 (53).

Compound **14**. Pale-yellow oil (Found: C, 81.6; H, 8.8. $C_{11}H_{14}O$ requires C, 81.44; H, 8.69%); ν_{max}(neat)/cm^{-1} 3300,

* Such as orobanone (4,5-cyclopentane-type annulation)[15a] and manicoline (4,5-cyclohexane-type annulation).[15b] Dehydrogenation of otherwise prepared **16**-type products led to 4,5-annelated troponoids.[2c] Moreover, oxidation of phenolic nitroalkanes led to 4,5-cyclopentane or 4,5-cyclohexane annelated tropones.[16]

2960, 2130 (HC≡C), 1720 (C=O), 1630 (C=C) and 1430; δ_C 18.09 (t, C-4'), 25.92 (t, C-3'), 27.86 (t, C-2'), 31.42 (t), 32.87 (t), 35.23 (t, C-5), 68.71 (d, C-6'), 83.74 (s, C-5'), 129.56 (d, C-2), 182.34 (s, C-3), 209.96 (s, C-1); δ_H 1.58 (quint, $J_{2',1'} = J_{2',3'}$ 6.9, 2'-H_2), 1.70 (quint, $J_{3',2'} = J_{3',4'}$ 6.9, 3'-H_2), 1.94 (t, $J_{6',4'}$ 2.7, 6'-H), 2.21 (td, $J_{4',3'}$ 6.9, $J_{4',6'}$ 2.7, 4'-H_2), 2.55 (t, $J_{1',2'}$ 6.9, 1'-H_2), 2.39 (m, 5-H_2), 2.57 (m, 4-H_2) and 5.95 (br quint, J 1.5, 2-H); *m/z* 162 ($M^{\cdot+}$, 47%), 133 (38), 119 (50), 105 (56), 91 (100), 81 (34), 67 (48) and 53 (47).

UV Irradiation of 3-(*Pent-4'-ynyl*)*cyclopent-2-enone* **13**.—(a) *In* MeCN *by the immersion-lamp method.* A solution of **13** (0.26 g, 1.78 mmol) in MeCN (130 cm^3) was irradiated for 3 or 4 h, corresponding to 21 or 41% conversion of **13**. Evaporation of the mixture at higher conversion, and FC of the residue with hexane–Et_2O (8:2), led to a mixture whose ^1H NMR spectrum revealed the presence of **16**, tricyclo[3.3.2.$0^{1,5}$]dec-9-en-4-one **17**, tricyclo[5.3.0.$0^{3,7}$]decan-4-one **18a**, and tricyclo[3.3.2.$0^{1,5}$]-decan-4-one **19** in 3:1:7:1.5 ratios, while **15** was present in only 2% yield. Only **16** could be separated in pure form by HPLC with hexane–Pr^iOH (99:1), t_R 7.5 min (2 mg). In turn, the mixture at 21% conversion, freed of unchanged **13** by FC, showed **18a** and **16** as major and minor products, respectively.

(b) *In* MeCN *or* Me_2CO *by the external lamp method.* Two tubes each containing **13** (0.031 g, 0.2 mmol), one as a MeCN solution (8 cm^3) and the other one as a Me_2CO solution (8 cm^3), were irradiated simultaneously for 105 min, corresponding to 76 or 56% conversion of **13**, respectively. Work-up as above led to the isolation of **18a** in 51% yield, while the ^1H NMR spectrum revealed the presence of **18a**, **19** and **17** in a radio of *ca.* 10:2:1.

(c) *In* CD_3CN *by the external lamp method.* UV irradiation of **13** was carried out as in (b) above, with CD_3CN in place of MeCN, for 4 h, corresponding to 50% conversion of **13**. The ^1H NMR spectrum of the residue from evaporation of the irradiated mixture showed compounds **15**, **16**, **17**, 1,3-dideuteriotricyclo[5.3.0.$0^{3,7}$]decan-4-one **18b**, and **19**, in a ratio of *ca.* 2:2.2:1:1.6:1.2. FC and HPLC purification as above in (a) led to the enone **15** (hexane–Pr^iOH (96:4), t_R 10.5 min, 2 mg), the dienone **16** (3 mg), and a mixture (5 mg) of **17**, **18a** and **19**.

(d) *In* $(CD_3)_2CO$ *by the external lamp method.* Compound **13** (9.6 mg) in $(CD_3)_2CO$ (4 cm^3) was irradiated with an external lamp for 115 min, corresponding to 51% conversion of **13**. Since the geometry of the apparatus and the concentrations of reagents were different from the other cases above, the efficiency cannot be compared. The ^1H NMR spectrum (200 MHz) of the residue from evaporation of the irradiated mixture showed **18b** as the major product (which was confirmed by TLC) accompanied by *ca.* 6% of **17**; no trace of **16** could be detected. Signals for compound **19**, if present, must have been buried in the other signals.

Compound **15**. Oil; δ_H 1.50–1.80 (m, 6 H), 2.20–2.70 (series of m, 5-H_2, 6-H_2), 3.37 (br s, 3-H) and 5.75 (br s, 2-H); *m/z* 149 ($[M + H]^+$, 35%), 148 ($M^{\cdot+}$, 4), 121 (50), 120 (14), 93 (10), 91 (30) and 55 (20) [Found (HRMS): $(M + H)^+$, 149.0965 ± 0.0015. Calc. for $C_{10}H_{13}O$: (M + H), 149.0966].

Compound **16**. Colourless oil; δ_C 22.06 (t), 23.63 (t), 36.94 (t), 39.59 (t), 40.58 (t), 129.04 (d) and 138.34 (d), are the only detectable signals; δ_H 1.88 (quint, J 7.2, 6-H_2), 2.62 and 2.36 (series of m, 10-H_2, 9-H_2, 7-H_2 and 5-H_2), 5.99 (d, $J_{2,3}$ 12.0, 2-H) and 6.56 (d, $J_{3,2}$ 12.0, 3-H); *m/z* 148 ($M^{\cdot+}$, 100%), 120 (50), 91 (96), 79 (30), 77 (21) and 55 (11) (Found: M^+, 148.0889 ± 0.0015. Calc. for $C_{10}H_{12}O$: *M*, 148.0888).

Compound **17** (data obtained from a mixture with compounds **18a** and **19**); δ_C 23.77 (t), 27.60 (t), 28.78 (t), 32.30 (t), 41.09 (t), 137.27 (d) and 143.31 (d), as the only signals that could be detected; δ_H 1.40–2.20 (series of m, 9 H), 2.44 (ddd, J_{gem} 17.6, J 8.5, 1.6, 3-H), 3.23 (ddd, J_{gem} 17.8, J 11.6, 9.4, 3-H) and 6.08 and 6.31 (2 d, $J_{9,10}$ 2.6, 9- and 10-H); *m/z* 148 ($M^{\cdot+}$, 5%), 120 (7) and 93 (72).

Compound **18a** (data obtained from a 10:2:1 mixture of compounds **18a**, **19** and **17**). Colourless oil; δ_C 25.62 (t), 25.83 (t), 31.92 (t), 33.21 (t), 37.21 (t), 38.09 (t, C-5), 40.41 (d, C-1), 46.95 (d, C-3), 52.87 (s, C-7) and 222.63 (s, C-4); δ_H 1.50–1.90 (m, 10 H), 2.21 (br ddd, J 10.5, 4.4, 2.0, 3-H), 2.34 (dddd, $J_{5a,5b}$ 17.9, J 7.1, 2.9, 2.0, 5-Ha), 2.51 (br dd, J 14.3, 6.4, 1-H) and 2.77 (tddd, $J_{5b,5a}$ 17.9, J 12.5, 9.5, $J_{5b,3}$ 0.8, 5-Hb); *m/z* 150 ($M^{\cdot+}$, 48%), 122 (58), 95 (61) and 81 (42) (Found: M^+, 150.1044 ± 0.0015. Calc. for $C_{10}H_{14}O$: *M*, 150.1045).

Compound **18b** (data obtained from a mixture with compounds **17** and **19**); δ_C 25.65 (t), 25.71 (t), 31.92 (t), 33.12 (t), 37.23 (t) and 38.10 (t); δ_H 1.40–1.85 (series of m, 10 H), 2.34 (ddt, J_{gem} 17.5, J 7.6, 2.4, 5-Ha) and 2.77 (ddd, J_{gem} 17.5, J 12.0, 9.2, 5-Hb); *m/z* 152 ($M^{\cdot+}$, 2%), 124 (2), 97 (4) and 83 (3).

Compound **19** (data obtained from a mixture with compounds **17** and **18b**); δ_C 25.01 (t), 28.13 (t), 29.41 (t), 32.31 (t), 33.51 (t), 39.95 (t) and 40.97 (t); δ_H 1.40–2.15 (series of m, 12 H), 2.46 (ddd, J_{gem} 17.7, J 8.9, 3.8, 3-H) and 2.92 (ddd, J_{gem} 17.7, J 10.6, 9.2, 3-H); *m/z* 150 ($M^{\cdot+}$, 1%), 122 (1) and 95 (3).

UV Irradiation of 3-(*Hex-5-ynyl*)*cyclopent-2-enone* **14**.—A solution of compound **14** (0.12 g, 0.77 mmol) in MeCN (140 cm^3) was irradiated with the immersion lamp for 4 h to give up to 53% conversion of **14**. Evaporation and preparative TLC with light petroleum (b.p. 60–80 °C)–Et_2O (3:2) led to tricyclo[5.4.0.$0^{3,7}$]undec-1-en-4-one **20** (R_F 0.51, 8.2 mg, 12% yield) and tricyclo[4.3.2.$0^{1,6}$]undec-10-en-7-one **21** (R_F 0.61; 16.0 mg, 24%). No products of 1,2-acyl shift could be observed.

Compound **20**. Oil (Found: C, 81.6; H, 8.85. $C_{11}H_{14}O$ requires C, 81.44; H, 8.7%); δ_C 19.15 (t), 21.96 (t), 25.60 (t), 26.96 (t); 31.92 (t), 35.82 (t), 61.30 (d) and 122.21 (d); δ_H 1.60–2.50 (series of m, 11 H), 2.73 (br s, 3-H), 2.84 (dddd, J_{gem} 17.7, J 11.7, 9.3, 1.2, 5-H) and 5.67 (dd, J 1.8, 0.9, 2-H); *m/z* 163 ($[M + H]^+$, 19%), 162 ($M^{\cdot+}$, 4), 135 (12), 134 (5), 107 (14), 105 (22), 93 (16), 91 (39), 67 (24), 57 (26) and 55 (37).

Compound **21**. Oil; δ_C 19.63 (t), 19.91 (t), 23.65 (t), 27.25 (t), 32.43 (t), 35.14 (t), 58.61 (s), 71.90 (s), 139.07 (d) and 146.18 (d); δ_H 1.40–2.40 (series of m, 11 H), 2.94 (ddd, J_{gem} 17.7, J 12.0, 9.3, 8-H), 6.06 and 6.32 (2 d, $J_{10,11}$ 2.7, 10- and 11-H); *m/z* 162 ($M^{\cdot+}$, 16), 134 (29), 120 (19), 107 (27), 105 (38), 93 (27), 91 (100), 79 (45), 77 (43), 67 (24), 57 (32) and 55 (30) (Found: M^+, 162.1043 ± 0.0015. Calc. for $C_{11}H_{14}O$: *M*, 162.1044).

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References

1 M. Demuth, in *Comprehensive Organic Synthesis*, ed. B. M. Trost and I. Fleming, vol. 5, p. 215, Pergamon Press, Oxford, 1991.
2 (*a*) M. Cavazza and F. Pietra, *J. Chem. Soc., Perkin Trans. 1*, 1985, 2283; (*b*) M. Cavazza, A. Guerriero and F. Pietra, *J. Chem. Soc., Perkin Trans. 1*, 1986, 2005; (*c*) M. Cavazza and F. Pietra, *J. Chem. Soc., Chem. Commun.*, 1986, 1480.
3 (*a*) D. Hirschi, W. Luef, P. Gerber and R. Keese, *Helv. Chim. Acta*, 1992, **75**, 1897; P. Gerber and R. Keese, *Tetrahedron Lett.*, 1992, **33**, 3987; (*b*) E. R. Koft and A. B. Smith, III, *J. Am. Chem. Soc.*, 1984, **106**, 2115; M. C. Pirrung and S. A. Thomson, *Tetrahedron Lett.*, 1986, **27**, 2703; (*c*) E. R. Koft and A. B. Smith, III, *J. Org. Chem.*, 1984, **49**, 832; (*d*) T. Z. Wang and L. A. Paquette, *J. Org. Chem.*, 1986, **51**, 5232.
4 R. Criegee and H. Furrer, *Chem. Ber.*, 1964, **97**, 2949.
5 S. Fujikura, M. Inone, K. Utimoto and H. Nozaki, *Tetrahedron Lett.*, 1984, **25**, 1999.

6 H. P. Knoess, M. T. Furlong, M. J. Rozema and P. Knochel, *J. Org. Chem.*, 1991, **56**, 5974.
7 E. F. De Medeiros, J. M. Herbert and R. J. Taylor, *J. Chem. Soc., Perkin Trans. 1*, 1991, 2725 and references therein.
8 E. Piers, J. R. Grierson, C. Kun Lau and I. Nagakura, *Can. J. Chem.*, 1982, **60**, 210.
9 S. Hussain, D. I. Shuster and El-Bayoumy, *Tetrahedron Lett.*, 1982, **23**, 153.
10 E. P. Serebryakov, S. D. Kulomzina-Pletneva and A. K. Margaryan, *Tetrahedron*, 1979, **35**, 77.
11 A. R. Matlin, C. F. George, S. Wolff and W. C. Agosta, *J. Am. Chem. Soc.*, 1986, **108**, 3385.
12 (*a*) R. G. Cargill, J. R. Damewood and M. M. Cooper, *J. Am. Chem. Soc.*, 1966, **88**, 1330; (*b*) R. L. Cargill and A. B. Sears, *Tetrahedron Lett.*, 1972, **34**, 3555.
13 R. L. Cargill, D. M. Pond and S. O. Le Grand, *J. Org. Chem.*, 1970, **35**, 359.
14 R. L. Cargill, M. E. Beckhman, A. E. Siebert and J. Dorn, *J. Org. Chem.*, 1965, **30**, 3647.
15 (*a*) A. Fruchier, J. P. Rascol and C. Andary, *Phytochemistry*, 1981, **20**, 777; (*b*) J. Polonsky, J. Varenne, T. Prangé, C. Pascard, H. Jacquemin and A. Fournet, *J. Chem. Soc., Chem. Commun.*, 1981, 731.
16 A. S. Kende and K. Koch, *Tetrahedron Lett.*, 1986, **27**, 6051.
17 D. H. Doddrell, D. T. Pegg and H. R. Bendall, *J. Magn. Reson.*, 1982, **48**, 323.
18 A. Bax, R. Freeman and G. Morris, *J. Magn. Reson.*, 1981, **42**, 164.
19 A. Bax, *J. Magn. Reson.*, 1983, **53**, 517; K. Kessler, C. Criesinger, J. Zarbock and H. R. Loosli, *J. Magn. Reson.*, 1984, **57**, 331.

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