174. Photoinduced Double Addition of Acetylene to 3-Oxocyclopent-1-ene-1-carbonitrile or 3-Oxocyclopent-1-enyl Acetate Leading to 2,3-Dihydro-1*H*-inden-1-one and Other Rearranged Products

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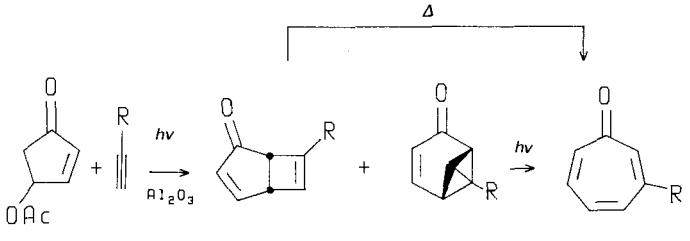
(30. V. 88)

UV Irradiation of 3-oxocyclopent-1-enyl acetate (**17**) and acetylene in MeCN at 0° gives, besides the product of normal enone-alkyne [2 + 2] cycloaddition (*cis*-4-oxobicyclo[3.2.0]hept-6-en-1-yl acetate, **18**) and its product of oxa-di-π-methane rearrangement (5-oxotricyclo[4.1.0.$0^{2,7}$]hept-2-yl acetate, **19**), unexpected products of further addition of a molar equivalent of acetylene. These are indanone (= 2,3-dihydro-1*H*-inden-1-one, **16**), in 21% yield, *cis*-1-*cisoid*-1,2-*cis*-2- (**20**) and *cis*-1-*transoid*-1,2-*cis*-2-7-oxotricyclo[4.3.0.$0^{2,5}$]non-3-en-1-yl acetate (**21**), 4-oxo-7-*'exo'*-vinyltricyclo[3.2.0.$0^{2,6}$]hept-2-yl acetate (**22**), *cis*-4-oxo-6-*'endo'*- (**23**) and *cis*-4-oxo-6-*'exo'*-vinylbicyclo[3.2.0]hept-1-yl acetate (**24**), and *cis*-4-oxo-7-*'exo'*-vinylbicyclo[3.2.0]hept-1-yl acetate (**25**). At least in part, indanone must be formed *via* intermediates **20** and **21**. In fact, on heating a 9:1 mixture **20**/**21**, indanone is obtained quantitatively. With 3-oxocyclopent-1-ene-1-carbonitrile (**15**) in place of **17**, indanone is formed in lower (8%) yield besides much tars.

1. Introduction. – We have recently exploited the [2 + 2] photocycloaddition of alkynes **2** and **7** with cyclopent-2-enones **1**, **6**, and **10** for the synthesis of natural 3-alkyl- (**5**) *(Scheme 1)* [1] and 4-alkyltropones (**11**, *Scheme 2*) [2] and of γ-tropolone (2-hydroxy-2,4,6-cycloheptatrien-1-one, **14**; *Scheme 3*) [3]. Observed [1] [2] or not [3], in all such cases bicyclo[3.2.0]heptadiene- or -heptene-type cycloadducts, such as **3** and **8**, must be the first formed intermediates which, then, undergo either light-induced oxa-di-π-methane rearrangement to give the tricyclic compounds **4** [1] or **9** [2], or direct ring expansion to cylcoheptadienes **13** [3].

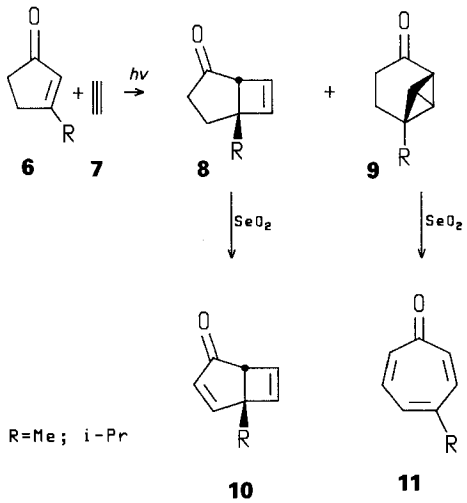
Scheme 1



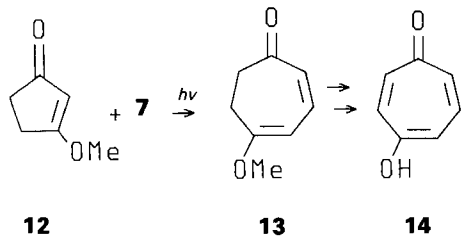
1 **2** **3** **4** **5**

R = Bu; C(OH)Me$_2$

Scheme 2



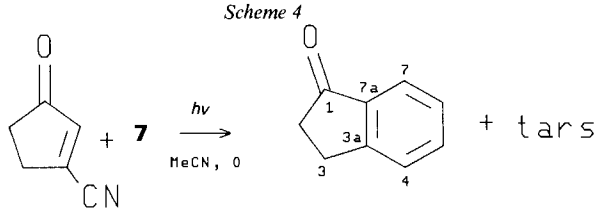
Scheme 3



Continuing our investigations on the use of enone-alkyne cycloaddition reactions for the synthesis of cycloheptenones and troponoids, we report here the unprecedented observation that certain cyclopentenones undergo double addition of acetylene under UV irradiation.

2. Results and Discussion. – UV irradiation ($\lambda \geq 280$ nm) of a solution of 3-oxocyclopent-1-en-1-carbonitrile (**15**) and acetylene (**7**) in MeCN at 0° affords neither a primary cycloadduct of type **8** nor its product of oxa-di-π-methane rearrangement **9**. The only defined product which can be isolated, besides much tars, is indanone (**16**), albeit in a low

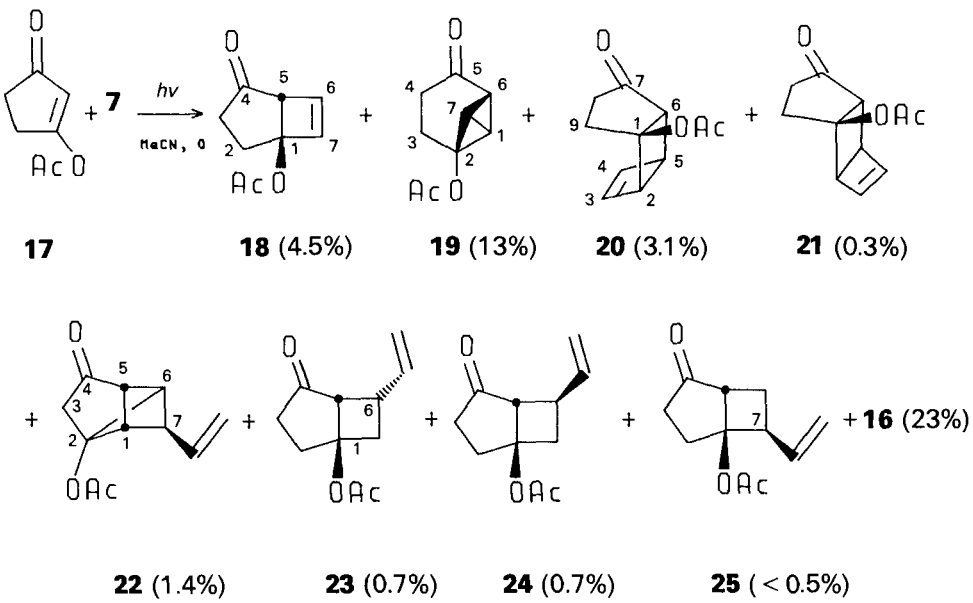
Scheme 4



(8%) yield *(Scheme 4)*. Formation of indanone must involve incorporation of two molecules of acetylene into **15**.

Changing to 3-oxocyclopent-1-enyl acetate (**17**), under similar conditions, the expected primary cycloadduct **18** and its rearranged photoproduct **19** are formed, though in mixture with a large amount of indanone (**16**) and small amounts of a variety of rearranged products which also must involve incorporation of two molecules of acetylene into the cyclopentenone precursor *(Scheme 5)*. The rearranged products are formally of three types: of [2 + 2] cycloaddition of acetylene to **18** (**20** and **21**), of addition of acetylene to **18** with reduction (**23**, **24**, and **25**), and, finally, of rearrangement of **20** and **21** (**22**).

Scheme 5



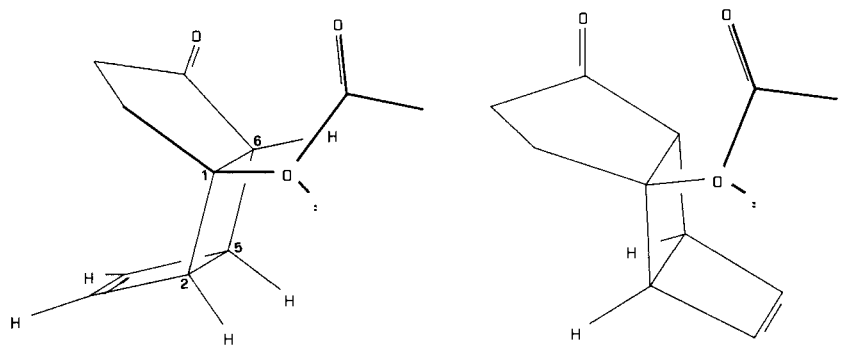
17 **18** (4.5%) **19** (13%) **20** (3.1%) **21** (0.3%)

22 (1.4%) **23** (0.7%) **24** (0.7%) **25** (< 0.5%)

+ **16** (23%)

As, to our knowledge, reaction of a cyclopentenone with 2 mol-equiv. of acetylene is unprecedented, a detailed investigation of the structure of the reaction products was warranted. Structures **18** and **19** are immediately established by comparison of spectral data with close analogues [1–3]. The other structures in *Scheme 5* are derived as follows. ^{1}H-NMR data for compounds **20** and **21** reveal a β-AcO-substituted cyclopentanone and a cyclobutene ring as with **18**. However, there are resonances for two more CH groups, and the olefinic protons are not coupled to H–C–C=O. This, and the need to accommodate three cycles, which is indicated by both the composition $C_{11}H_{12}O_3$ and the presence of a C=O and an olefinic bond, suggests structures **20** and **21**.

The *cisoid*-configuration for **20** rests on both large coupling [4] and NOE enhancement (14%) between the H–C(5) and H–C(6). With **21**, H–C(5) and H–C(6) reveal a smaller mutual coupling and no NOE, so that the *transoid*-configuration is assumed. Such conclusions are based on dihedral angles and H···H distances derived for **20** and **21** from molecular-mechanics calculations [5] *(Fig. 1)*.



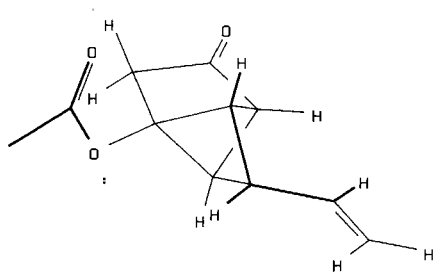
20 **21**

Fig. 1. *Minimum-energy geometries for* **20** *and* **21** *according to molecular-mechanics calculations*

Products **23**, **24**, and **25** have two H-atoms more than **20** and **21**, from which they also differ in the absence of the characteristic ^{1}H-NMR cyclobutene signals, which are replaced by vinyl signals. The assignment of H–C(6) is based on coupling with C*H*=CH$_2$; further coupling also allows to assign the protons at C(5).

The configuration assignments of **23**, **24**, and **25** are based on larger ^{1}H,^{1}H couplings between *cis*- than *trans*-cyclobutane protons [4]. Thus, J(5,6) is larger for **23** than for **24**, which allows us to assign the vinyl group to the *'endo'*-position in **23** and the *'exo'*-position in **24**. For **25**, H$_\beta$–C(6) is assigned on the basis of its large coupling with H–C(5); the relatively small coupling of H$_\beta$–C(6) with H–C(7) indicates that the vinyl group occupies the *'exo'*-position.

Compound **22** is isomeric with **20** and **21** and, from the presence of a C=O and a C=C bond, it must be tricyclic. There is a vinyl group, but, in contrast with **23**–**25**, the CH$_2$ group shows no ^3J couplings and is only slightly coupled to H–C(5). All NMR data are in accordance with a bicyclic system of the type of compounds **23**–**25**, with C(2) linked to C(6) and with the AcO group relocated to C(2). Though ^{1}H,^{1}H coupling constants are difficult to rationalize in this case, NOE experiments are revealing when evaluated on the basis of the minimized structure **22** in *Fig. 2*, which is derived from molecular-mechanics calculations [5]. Thus, NOE's of 7% between H–C(1) and H–C(5) and of 16% between H–C(6) and H–C(7) firmly establish the C(1)–C(5) and C(6)–C(7) connectivities. Moreover, that the vinyl group is at C(7) is supported by a 14% NOE between C*H*=CH$_2$ and H–C(5).

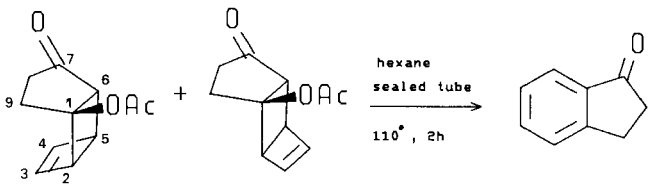


22

Fig. 2. *Minimum-energy geometry for* **22** *according to molecular-mechanics calculations*

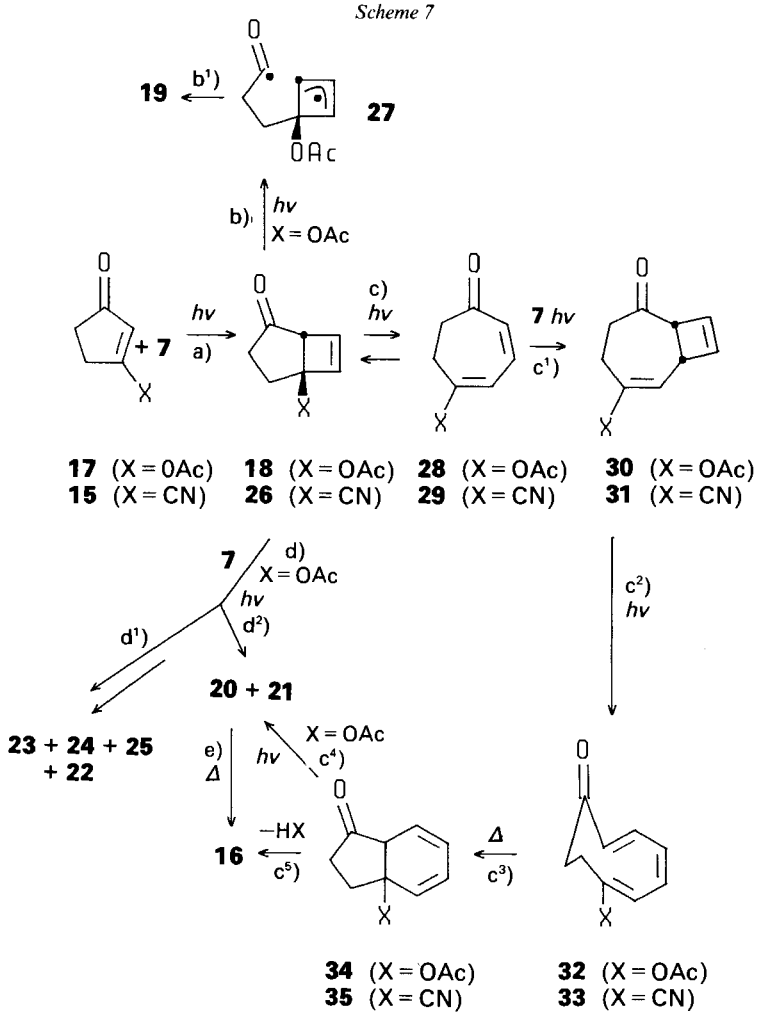
Mechanistically significant is the fact that heating of a 9:1 mixture **20**/**21** in hexane in a sealed tube leads quantitatively to indanone (**16**, *Scheme 6*). On this basis, we envisage two alternative routes, that center on **20** and **21**, to **16** from cyclopent-2-en-1-one precursors *(Scheme 7)*.

Scheme 6



20 **21** **16** (100%)

Scheme 7



17 (X = OAc) **18** (X = OAc) **28** (X = OAc) **30** (X = OAc)
15 (X = CN) **26** (X = CN) **29** (X = CN) **31** (X = CN)

34 (X = OAc) **32** (X = OAc)
35 (X = CN) **33** (X = CN)

The isolated intermediates **18**, **20**, **21**, and the hypothetical intermediates **28**, **30**, **32**, **34** lie along the longer pathway ($a + c + c^1 + c^2 + c^3 + c^4 + e$) from the acetate **17** to **16**, whereas the hypothetical intermediates **26**, **29**, **31**, **33**, and **35** lie along the parallel pathway from nitrile **15** to **16**.

With acetate **17**, the shorter pathway ($a + d + d^2 + e$) to **16** is envisaged as starting from the same intermediate **18**. We favor the above pathway, however, since stage c^1 represents a classical enone-alkyne photocycloaddition [1] [3], while the photochemical disrotatory electrocyclic reaction of stage c is precedented [6]. Moreover, stages of type c^3 and c^4 have been observed with cyclic olefins [7].

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Experimental Part

1. *General.* Yields for the condensations are given on reacted compounds. UV irradiations were carried out with a 125-W-*Pyrex*-filtered medium-pressure immersion Hg, using a cylindrical reactor of 6.5-cm diameter. Yields are calculated on reacted starting material. TLC: *Merck-Si*$_{F254}$ plates. HPLC and reverse-phase HPLC: 25 × 1-cm columns filled with *Merck-LiChrosorb Si-60* (5 μm) and *Merck-LiChroprep RP-8* (5 mμ), respectively, UV monitoring at λ 215 nm. IR spectra: *Perkin-Elmer 337* spectrometer (ν_{max} in cm^{-1}). Molecular-mechanics calculations were carried out with the MMPMI program by *Serena Software*, Bloomington, Indiana. NMR: *Varian 360* (60 MHz) or *Varian XL-300* spectrometer (^1H at 300 MHz, ^{13}C at 75.4 MHz). ^1H-NMR data: at 300 MHz in $CDCl_3$, unless otherwise stated, δ (ppm) relative to internal TMS (= 0 ppm) and J in Hz. Analysis of ^1H-NMR spectra is based on experiments of differential decoupling spectroscopy. For ^{13}C-NMR, multiplicities from APT [8]; assignments of compound **20** by selective heteronuclear decoupling and of compound **22** by HECTOR [9]. MS (EI; *m/z* (%)) home-built spectrometer based on the *ELFS-4-162-8-Extranuclear* quadrupole [10].

2. *3-Oxocyclopent-1-ene-1-carbonitrile* (**15**). 2-(Phenylseleno)cyclopent-2-en-1-one, obtained according to [11], was transformed in 69% yield according to [12] into 3-oxo-2-(phenylseleno)cyclopentane-1-carbonitrile, 0.9 g (3.5 mmol) of which in 4 ml of CH_2Cl_2 and 0.56 ml of pyridine at 0° were added to 0.8 ml of 30% H_2O_2. After 20 min at r.t., the mixture was extracted with Et_2O, washed in turn with 0.1M HCl and with H_2O, and then dried (Na_2SO_4). Evaporation and TLC of the residue with petroleum ether/AcOEt 3:2 led to 0.37 g (99%) of **15** (R_f 0.48) as a colourless oil which tends to darken on standing. IR (neat): 2235 (CN), 1722 (CO). ^1H-NMR ($CDCl_3$, 60 MHz): 6.65 (*t*, J = 1.7, H–C(2)); 2.70 (*m*, 2 H–C(4)); 2.25 (*m*, 2 H–C(5)). Anal. calc. for C_6H_5NO: C 67.28, H 4.70; found: C 67.10, H 4.60.

3. *Photoreaction of* **15** *with Acetylene* (**7**). A soln. of **15** (0.2 g, 1.87 mmol) in 130 ml of MeCN saturated with **7** at 0° was irradiated for 220 min, until 70% of the enone had disappeared with formation of much tars. Evaporation of the soln. and TLC of the residue with petroleum ether/Et_2O 1:1 led to 14 mg (8%) of *indanone* (= *2,3-dihydro-1H-inden-1-one*; **16**), R_f 0.48, identical in every respect to the commercial product *(Aldrich)*, besides 60 mg of unreacted **15**, R_f 0.29. The course of the irradiation was unaffected by the presence of 2 mmol of Et_3N.

Data of **16**. ^1H-NMR: in agreement with [13]. ^{13}C-NMR: 207.2 (*s*, C(1)); 36.10 (*t*, C(2)); 25.82 (*t*, C(3)); 155.21 (*s*, C(3a)); 123.75 (*d*, C(4)); 127.29 (*d*, C(5)); 134.30 (*d*, C(6)); 126.50 (*d*, C(7)); 137.01 (*s*, C(7a)). MS: 132 (M^+, 100), 104 ($M^+ - CO$).

4. *Photoreaction of 3-Oxocyclopent-1-enyl Acetate* (**17**) *with* **7**. A soln. of **17** [14] (0.46 g, 3.26 mmol) in 240 ml of MeCN at 0° was irradiated under continuous bubbling with **7**, while monitoring by HPLC *(Merck LiChrosorb RP8)* indicated the formation of **16** and the disappearance of **17** with the following results: conversion (%) of **17** (yield of **16**): 16 (8%); 19.2 (14.3%); 31 (18.5%); 42.7 (18.1%); 50 (19.6%); 55 (21% at 690 min). The mixture was subjected to TLC with petroleum ether/Et_2O 2:3 collecting the following bands: R_f 0.58 (49 mg of **16**, 21%), 0.48 (38 mg), 0.31 (40 mg of **19**, 13%), 0.16 (0.19 g, unreacted **17**). The material corresponding to R_f 0.48 was subjected to reverse-phase HPLC with MeCN/H_2O 45:55, to get **18** (t_R 6.0 min, 13 mg, 4.5%), a 9:1 mixture **20**/**21** (t_R 7.8 min, 10 mg), a mixture of **16** and **25** (t_R 8.4 min, 5 mg), and a mixture **22**/**23**/**24** (t_R 9.5 min); in all these cases, *to*

avoid loss of the volatile products, the eluates were partially evaporated and then extracted with pentane, which was then evaporated. HPLC with hexane/i-PrOH 96:4 allowed us to obtain pure **25** and **16** (t_R 6.5, < 0.5%, and 9.3 min, 2%, resp.), as well as pure **22**, **23**, and **24** (t_R 7.7, 1.4%, 8.3, 0.7%, and 9.8 min, 0.7%, resp.), whereas **20** could not be separated from **21**.

cis-*4-Oxobicyclo[3.2.0]hept-6-en-1-yl Acetate* (**18**). ^{1}H-NMR: 6.62 (*d*, $J(6,7) = 2.7$, H–C(7)); 6.29 (*dd*, $J(6,7) = 2.7$, $J(5,6) = 1.0$, H–C(6)); 3.24 (*m*, H–C(5)); 2.75 (*dddd*, $J = 17.8, 10.7, 9.2, 1.3$, H_{exo}–C(3)); 2.60, 2.06 (2*m*, H_{endo}–C(2), H_{exo}–C(2)); 2.49 (*dddd*, $J = 17.9, 11.0, 9.5, 1.3$, H_{endo}–C(3)); 2.07 (*s*, Ac). ^{13}C-NMR: 213.55 (*s*, C(4)); 170.34 (*s*, $COOCH_3$); 142.40 (*d*, C(7)); 138.44 (*d*, C(6)); 85.63 (*s*, C(1)); 58.98 (*d*, C(5)); 36.89 (*t*, C(3)); 28.33 (*t*, C(2)); 21.20 (*q*, $COOCH_3$). MS: 124 (30, M^+), 96 (30, $[M - CO]^+$), 95 (14, $[M - 29]^+$), 43 (100).

5-Oxotricyclo[4.1.0.0^{2,7}]hept-2-yl Acetate (**19**). ^{1}H-NMR: 2.73 (br. *d*, $J = 3.0$, H–C(1), H–C(7)); 2.55 (*t*, $J(1,6) = J(6,7) = 3.0$, H–C(6)); 2.28 (*m*, 2 H–C(3), 2 H–C(4)); 2.06 (*s*, Ac). MS: 151 (2, $[M - Me]^+$), 134 (20, $[M - CO]^{+\cdot}$), 123 (35, $[M - Ac]^+$).

cis-*1*-cisoid-*1,2*-cis-*2-7-Oxotricyclo[4.3.0.0^{2,5}]non-3-en-1-yl Acetate* (**20**). ^{1}H-NMR: 6.41 (*dd*, $J(3,4) = J(4,5) = 2.5$, H–C(4)); 6.24 (*dd*, $J(3,4) = J(2,3) = 2.5$, H–C(3)); 3.60 (*ddd*, $J(5,6) = 9.0$, $J(2,5) = 3.2$, $J(4,5) = 2.5$, H–C(5)); 3.55 (*dd*, $J(2,5) = 3.2$, $J(2,3) = 2.5$, H–C(2)); 3.15 (br. *d*, $J(5,6) = 9.0$, H–C(6)); 2.60 (*dddd*, $J = 16.7, 8.7, 4.7, 2.0$), 2.19 (*dddd*, $J = 16.7, 9.5, 7.3, 1.4$) (H_{exo}–C(8), H_{endo}–C(8)); 2.40, 2.07 (2*m*, H_{exo}–C(9), H_{endo}–C(9)); 2.08 (*s*, Ac). ^{13}C-NMR: 217.68 (*s*, C(7)); 170.15 (*s*, $COOCH_3$); 141.52 (*d*, C(3)); 137.65 (*d*, C(4)); 84.18 (*s*, C(1)); 51.75 (*d*, C(6)); 51.38 (*d*, C(2)); 42.90 (*t*, C(8)); 41.40 (*d*, C(5)); 31.71 (*t*, C(9)); 21.49 (*q*, $COOCH_3$).

cis-*1*-transoid-*1,2*-cis-*2-7-Oxotricyclo[4.3.0.0^{2,5}]non-3-en-1-yl Acetate* (**21**). ^{1}H-NMR: 6.37 (*dd*, $J(3,4) = J(4,5) = 2.5$, H–C(4)); 6.16 (*dd*, $J(3,4) = J(2,3) = 2.5$, H–C(3)); 3.65 (*m*, H–C(6)); 2.99 (*m*, H–C(5)); 2.78 (*m*, H–C(2)); 2.15 (*s*, Ac); the signals for 2 H–C(8) and 2 H–C(9) are submerged by the signals for the corresponding protons of **20**. ^{13}C-NMR: 217.68 (*s*, C(7)); 171.22 (*s*, $COOCH_3$); 141.98 (*d*, C(3)); 138.31 (*d*, C(4)); 83.15 (*s*, C(1)); 55.51 (*d*, C(2) or C(6)); 52.04 (*d*, C(2) or C(6)); 41.26 (*d*, C(5)); 38.08 (*t*, C(8)); 34.09 (*t*, C(9)); 21.03 (*q*, $COOCH_3$). MS of **20**/**21**: 150 (11, $[M - CH_2CO]^+$), 149 (29, $[M - Ac]^{+\cdot}$), 132 (38, $[M - AcOH]^+$), 121 (14), 104 (77), 91 (100), 82 (35), 69 (17), 43 (100).

4-Oxo-7-'exo'-*vinyltricyclo[3.2.0.0^{2,6}]hept-2-yl Acetate* (**22**). ^{1}H-NMR: 6.04 (*ddd*, $J(CH{=}CH_2, CH{=}CH_{trans}) = 17.9$, $J(CH{=}CH_2, CH{=}CH_{cis}) = 10.3$, $J(CH{=}CH_2, H{-}C(7)) = 7.6$, $CH{=}CH_2$); 5.27 (*ddd*, $J(CH{=}CH, CH{=}CH_{trans}) = 17.9$, $J_{gem} = J(H{-}C(7), CH{=}CH_{cis}) = 1.2$, 1 H, $CH{=}CH_2(trans)$); 5.25 (*ddd*, $J(H{-}C(6), CH{=}CH_{cis}) = 10.3$, $J_{gem} = J(H{-}C(7), CH{=}CH_{cis}) = 1.2$, 1 H, $CH{=}CH_2(cis)$); 3.89 (br. *ddd*, $J(5,6) = 6.6$, $J(3\alpha,5) \approx J(3\beta,5) = 1.3$, H–C(5)); 3.68 (br. *ddd*, $J(H{-}C(7), CH{=}CH_2) = 7.6$, $J(H{-}C(7), CH{=}CH_{trans}) \approx J(H{-}C(7), CH{=}CH_{cis}) = 1.2$, H–C(7)); 3.30 (*dd*, $J(5,6) = 6.6$, $J(1,6) = 0.6$, H–C(6)); 3.08 (br. *d*, $J(1,6) = 0.6$, H–C(1)); 2.32 (*dd*, $J_{gem} = 17.9$, $J(3\beta,5) = 1.3$, H_β–C(3)); 2.13 (*dd*, $J_{gem} = 17.9$, $J(3\alpha,5) = 1.3$, H_α–C(3)); 2.00 (*s*, Ac). ^{13}C-NMR: 211.90 (*s*, C(4)); 169.76 (*s*, $COOCH_3$); 131.44 (*d*, $CH{=}CH_2$); 119.55 (*t*, $CH{=}CH_2$); 74.61 (*s*, C(2)); 73.07 (*d*, C(6)); 61.86 (*d*, C(7)); 56.91 (*d*, C(5)); 37.64 (*d*, C(1)); 35.74 (*t*, C(3)); 20.92 (*q*, $COOCH_3$). MS: 150 (8, $[M^{+\cdot} - CH_2{=}CO]$), 133 (3, $[M^{+\cdot} - OAc]$), 132 (3, $[M - AcOH]^{+\cdot}$), 122 (4, [150 – CO]), 82 (35), 63 (17), 43 (100).

cis-*4-Oxo-6-*'endo'-*vinylbicyclo[3.2.0]hept-1-yl Acetate* (**23**). ^{1}H-NMR: 5.81 (*ddd*, $J(CH{=}CH_2, CH{=}CH_{trans}) = 16.7$, $J(CH{=}CH_2, CH{=}CH_{cis}) = 10.6$, $J(CH{=}CH_2, H{-}C(6)) = 6.0$, $CH{=}CH_2$); 5.14 (*ddd*, $J(CH{=}CH_2, CH{=}CH_{cis}) = 10.6$, $J_{gem} \approx J(H{-}C(6), CH{=}CH_{cis}) = 1.3$, 1 H, $CH{=}CH_2(cis)$); 5.09 (*ddd*, $J(CH{=}CH_2, CH{=}CH_{trans}) = 16.7$, $J_{gem} \approx J(H{-}C(6), CH{=}CH_{trans}) = 1.3$, 1 H, $CH{=}CH_2(trans)$); 3.43 (*m*, $J(5,6) = 11.4$, $J(6,7endo) = 6.0$, $J(6,7exo) = 9.8$, H–C(6)); 3.21 (br. *d*, $J(5,6) = 11.4$, H–C(5)); 2.73 (*dd*, $J_{gem} = 13.9$, $J(6,7exo) = 9.8$, H_{exo}–C(7)); 2.70–2.20 (*m*, 2 H–C(2), 2 H–C(3)); 2.50 (*dd*, $J_{gem} = 13.9$, $J(6,7endo) = 6.0$, H_{endo}–C(7)); 2.05 (*s*, Ac).

cis-*4-Oxo-6-*'exo'-*vinylbicyclo[3.2.0]hept-1-yl Acetate* (**24**). ^{1}H-NMR: 5.93 (*ddd*, $J(CH{=}CH_2, CH{=}CH_{trans}) = 17.2$, $J(CH{=}CH_2, CH{=}CH_{cis}) = 10.2$, $J(CH{=}CH_2, H{-}C(6)) = 6.8$, $CH{=}CH_2$); 5.07 (*ddd*, $J(CH{=}CH_2, CH{=}CH_{trans}) = 17.2$, $J_{gem} \approx J(H{-}C(6), CH{=}CH_{trans}) = 1.3$, 1 H, $CH{=}CH_2(trans)$); 5.05 (*ddd*, $J(CH{=}CH_2, CH{=}CH_{cis}) = 10.2$, $J_{gem} \approx J(H{-}C(6), CH{=}CH_{cis}) = 1.3$, 1 H, $CH{=}CH_2(cis)$); 2.87 (br. *d*, $J(5,6) = 6.6$, H–C(5)); 2.75–2.35 (superimposed *m*, 2 H–C(2), 2 H–C(3), 2 H–C(7)); 2.61 (*m*, H–C(6)); 2.02 (*s*, Ac). ^{13}C-NMR: 215.67 (*s*, C(4)); 170.15 (*s*, $COOCH_3$); 138.79 (*d*, $CH{=}CH_2$); 115.25 (*t*, $CH{=}CH_2$); 78.65 (*s*, C(1)); 58.05 (*d*, C(5)); 39.98 (*t*, C(3)); 38.65 (*t*, C(7)); 34.74 (*d*, C(6)); 34.06 (*t*, C(2)); 21.30 (*q*, $COOCH_3$). MS: 194 (1, M^+), 167 (2, $[M - CH{=}CH_2]^+$), 152 (24, $[M - CH_2{=}CO]^{+\cdot}$), 134 (13, $[M - AcOH]^{+\cdot}$), 124 (6, [152 – CO]), 43 (100).

cis-*4-Oxo-7-*'exo'-*vinylbicyclo[3.2.0]hept-1-yl Acetate* (**25**). ^{1}H-NMR: 5.95 (*ddd*, $J(CH{=}CH_2, CH{=}CH_{trans}) = 16.7$, $J(CH{=}CH_2, CH{=}CH_{cis}) = 10.5$, $J(CH{=}CH_2, H{-}C(7)) = 8.5$, $CH{=}CH_2$); 5.13 (*ddd*, $J(CH{=}CH_2, CH{=}CH_{cis}) = 10.5$, $J_{gem} \approx J(H{-}C(7), CH{=}CH_{cis}) = 1.3$, 1 H, $CH{=}CH_2(cis)$); 5.12 (*ddd*,

$J(CH{=}CH_2, CH{=}CH_{trans}) = 16.7$, $J_{gem} \approx J(H{-}C(7), CH{=}CH_{trans}) = 1.3$, 1 H, $CH{=}CH_2(trans)$); 3.16 (br. *ddd*, $J(H{-}C(7), CH{=}CH_2) = 8.5$, $J(H_{endo}{-}C(6), H{-}C(7)) = 7.5$, $J(H_{exo}{-}C(6), H{-}C(7)) = 3.6$, H–C(7)); 3.08 (br. *dd*, $J(H{-}C(5), H_{endo}{-}C(6)) = 7.5$, $J(H{-}C(5), H_{exo}{-}C(6)) = 11.1$, H–C(5)); 2.65–2.40 (*m*, 2 H–C(2), 2 H–C(3)); 2.21 (*ddd*, $J_{gem} = 15.2$, $J(H_{exo}{-}C(6), H{-}C(7)) = 3.6$, $J(H{-}C(5), H_{exo}{-}C(6)) = 11.1$, H_{exo}–C(6)); 2.01 (*s*, Ac); 1.99 (*ddd*, $J_{gem} = 15.2$, $J(H_{endo}{-}C(6), H{-}C(7)) \approx J(H{-}C(5), H_{endo}{-}C(6)) = 7.5$, H_{endo}–C(6)). ^{13}C-NMR: 136.2 (*d*, $CH{=}CH_2$); 116.9 (*t*, $CH{=}CH_2$); 55.1 (*d*, C(5)); 50.00 (*d*, C(7)); 40.15 (*t*, C(3)); 40.15 (*t*, C(6)); 34.20 (*t*, C(2)); 20.42 (*q*, $COOCH_3$); C(1) and C(4) not detected. MS: 152 (47, $[M - CH_2{=}CO]^+$), 134 (5, $[M - AcOH]^+$), 98 (22), 71 (23), 43 (100).

5. *Thermal Rearrangement of* **20** *and* **21**. The above mixture **20**/**21** (3 mg, 0.6 ml) was sealed in a *Pyrex* tube in 1 ml of hexane and heated at 110° for 2 h. The solvent was evaporated and the residue was taken in $CDCl_3$; ^{1}H-NMR revealed the presence of **16** (70%) and unreacted starting mixture (30%) as the only detectable signals.

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