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Photochemical 1,3-Acyl Shifts in Natural Product Synthesis

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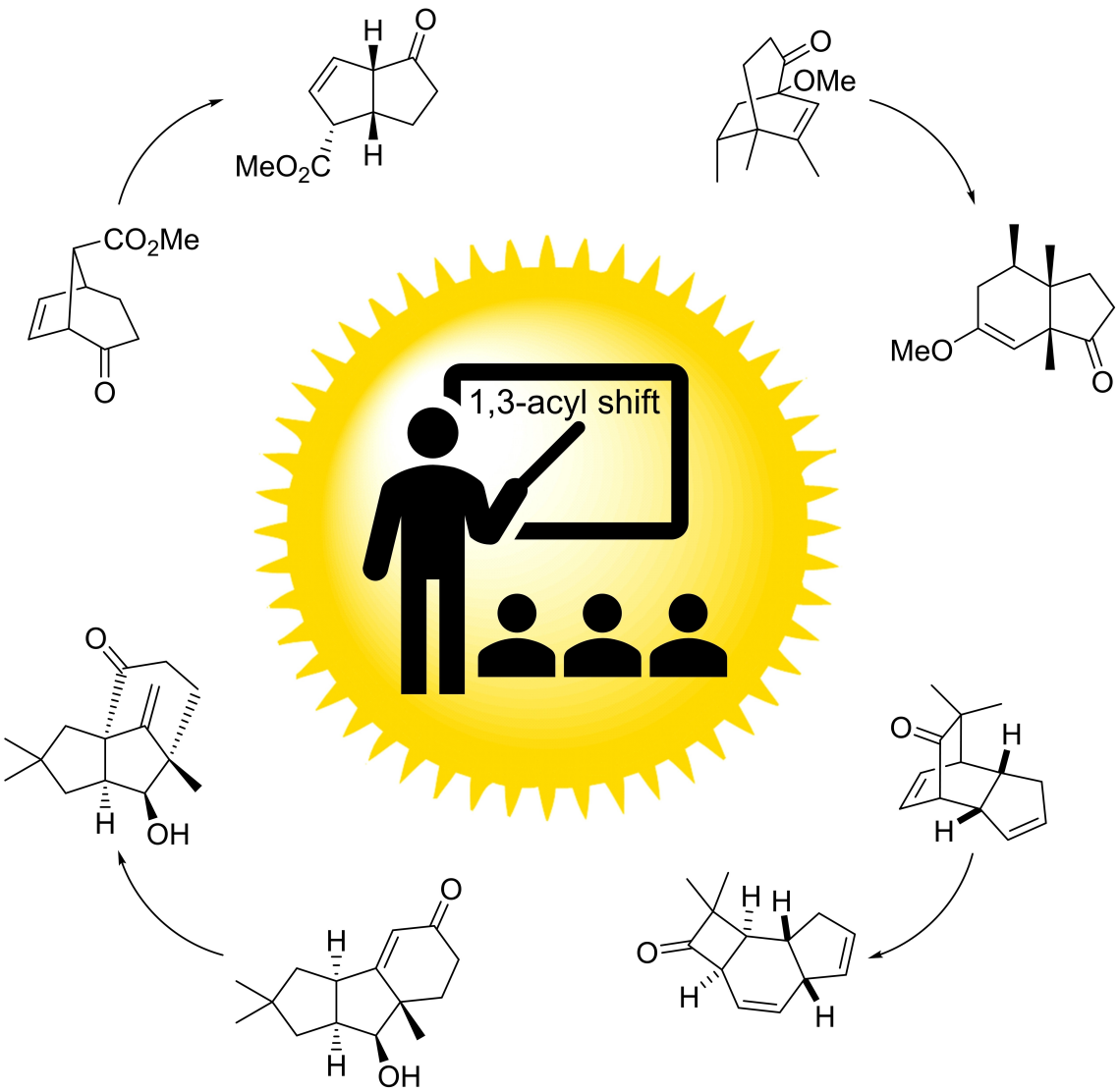
Dedicated to Prof. Cesare Gennari on the occasion of his 70th birthday.



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Photochemical, sigmatropic 1,3-acyl shifts represent a powerful tool to construct quaternary carbon atoms and the backbones of complex natural products which cannot be constructed easily by conventional methods. This review highlights applications of 1,3-acyl shifts to elegant, partly biomimetic total syntheses of natural products by discussing the underlying photochemical equilibrium.

1. Introduction

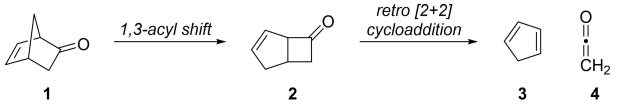
In 1963, sigmatropic 1,3-acyl shifts were described by Schenck and Schuster independently as photochemical fragmentation of dehydronorcamphor (**1**) to cyclobutanone **2** (Scheme 1).[1] Subsequent retro [2+2] cycloaddition of **2** led to cyclopentadiene **3** and ketene **4**.[1] Since then photochemical 1,3-acyl shifts have been discussed to occur either through a concerted or a diradical mechanism. Up to this date, the literature comprises only a few syntheses of natural products that muster a 1,3-acyl shift. The chosen strategies bypass the use of protecting groups and contain a favorable redox-economy.[2] The carbon atoms of the targeted structure are in most cases already assembled prior to the photochemical 1,3-acyl shift.

2. Mechanistic Considerations

Photochemical 1,3-acyl shifts of β,γ-unsaturated ketones are initiated by n-π*-absorption of a photon and excitation into the S_1 state from which the T_1 state is accessible by intersystem crossing (ISC, *i.e.* a spin flip) (Figure 1a–c).[3] The subsequent Norrish type I reaction can occur from both excited states.[4] Allylic rearrangement and recombination of the radical pair complete the 1,3-acyl shift (Scheme 2). The highly reactive radical pair may additionally enter other pathways for stabilization *e.g.* decarbonylation.[5] Further by-products can arise upon Norrish-Yang cyclization[6] initiated by a Norrish type II reaction.[7] Undesired *cis-trans* isomerization can be prevented if the alkene moiety is contained in a ring of six or less atoms (*vide infra*). 1,3-Acyl shifts are observed to occur primarily from the S_1 state whereas the oxa-di-π-methane rearrangement (1,2-acyl shift) occurs from the T_1 state to furnish the corresponding cyclo-propanes (Figure 1d).[8,9] Consequently, the reaction pathway can be controlled by the addition of triplet-sensitizers.[9]

Computational studies by Robb and co-workers in 1996 describe the transformation of **8** to **9** more narrowly as two competing extremes of the same mechanism (Scheme 2).[10] Pathway I proceeds *via* a stepwise fragmentation-recombination-mechanism in which the free radical pair **10** recombines to **9**. Pathway II is quasi-concerted, stereospecific, and contains a four-membered biradical which can either form a tight intermediate **11** in which all C–C bonds are fully formed or a loose intermediate **12** *e.g.* a radical pair held together in a solvent cage.

In 1969, Paquette and Meehan elucidated the photochemical equilibrium of the fused and bridged 1,3-enones **13** to **16** (Figure 2).[11] Upon irradiation the equilibrium shifted rapidly to a photo stationary state in which the fused isomers **13** and **15** exceeded their bridged counterparts **14** and **16** independently of which isomer was initially submitted to irradiation. Concom-



Scheme 1. 1,3-Acyl shift observed in the photochemical fragmentation of dehydronorcamphor (**1**) by Schenck and Schuster.[1]

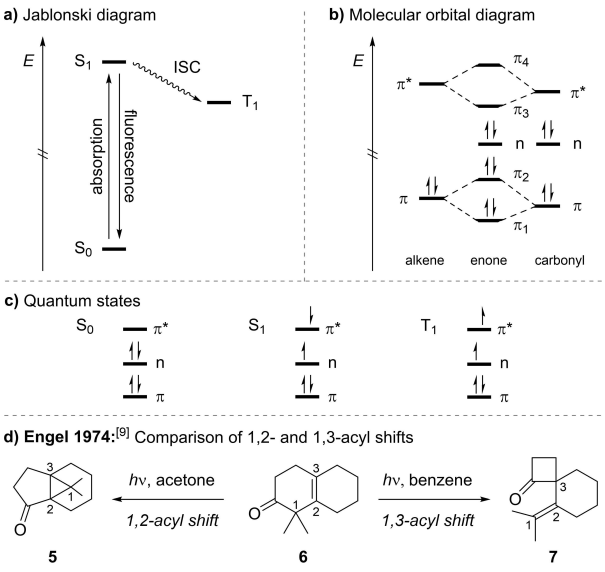


Figure 1. a) Jablonski diagram; b) molecular orbital diagram of an enone; c) quantum states of S_0, S_1 and T_1 states; d) comparison of photochemical 1,2- and 1,3-acyl shifts by Engel.[9] Acetone is a triplet-sensitizer. ISC = intersystem crossing.

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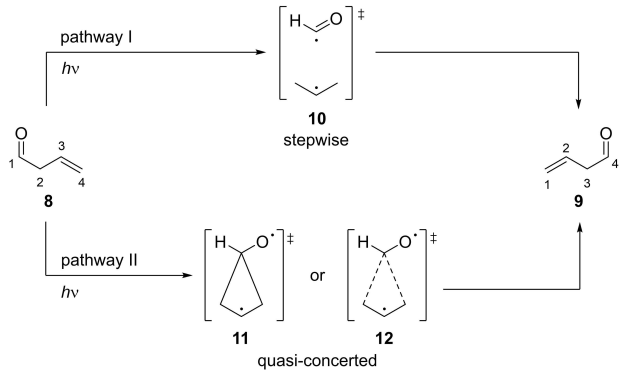

Scheme 2. Reaction mechanism of 1,3-acyl shifts proposed by Robb,[10] in 1996. Pathway I and II are two extremes of the same mechanism.

itantly with the thermodynamic stabilities of both isomers, it is assumed that their photochemical properties have an influence on the product distribution as well.[11–13] The non-planar β,γ-unsaturated ketone has an enhanced n-π*-transition due to the overlap of the non-bonding p-orbital of the carbonyl oxygen atom with the π-orbital of the alkene.[14] Furthermore, the absorption maxima λ_{max} of both isomers can be very similar (Figure 2) hence they are both excited with commonly employed mercury vapor lamps (principle emission 200–400 nm).[11,13] Consequently, both rearrangements (fused to bridged and bridged to fused) take place simultaneously with the n-π*-absorption of the bridged 1,3-enone occurring statistically more frequently due to the enhanced n-π*-absorption based on inherent stereoelectronic effects.

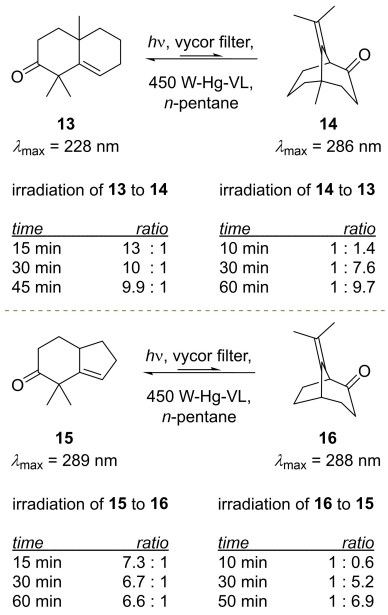

Figure 2. Photochemical equilibria studied by Paquette and Meehan.[11] The concentration of the bridged isomers exceed the concentration of the fused isomers. VL = vapor lamp.

3. Applications in Total Syntheses

Key steps in the total syntheses of natural products are designed to construct the carbon backbone in a highly elegant and efficient manner.[15] The significance of photochemical 1,3-acyl shifts to this purpose is demonstrated mainly in examples towards the intricate architecture of terpenes. To limit undesired side reactions upon photochemical excitation Pyrex®

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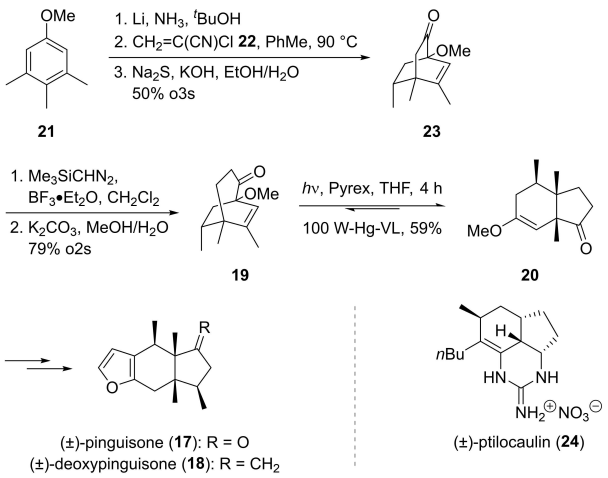
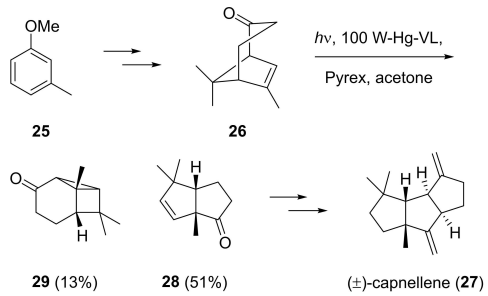
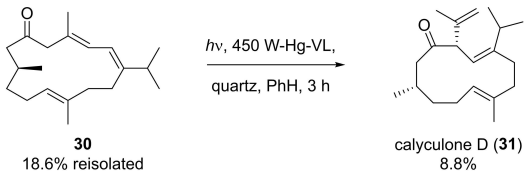
and Vycor® filters are commonly employed.[16] The first application of 1,3-acyl shifts to total synthesis was reported in 1986 by Kato *et al.* in the syntheses of (±)-pinguisone (**17**) and (±)-deoxypinguisone (**18**) (Scheme 3).[17] A photochemical 1,3-acyl shift from **19** to **20** was employed to construct the majority of the carbon skeleton of the natural products in 59% upon irradiation. Starting from anisole **21** a sequence of Birch reduction, a Diels-Alder reaction with α-chloroacrylonitrile **22** and hydrolysis[18] furnishes ketone **23**. Ring expansion with a Tiffeneau-Demjanov rearrangement gives rise to precursor **19**. A slightly modified route also granted access to (±)-ptilocaulin (**24**).[19]



Scheme 3. Syntheses of (±)-pinguisone (**17**), (±)-deoxypinguisone (**18**) and (±)-ptilocaulin (**24**) by Kato and co-workers from 1986 to 1988.[17,19] VL = vapor lamp.



Scheme 4. Yamamoto's synthesis of (±)-capnellene (**27**) in 1989.[20] VL = vapor lamp.

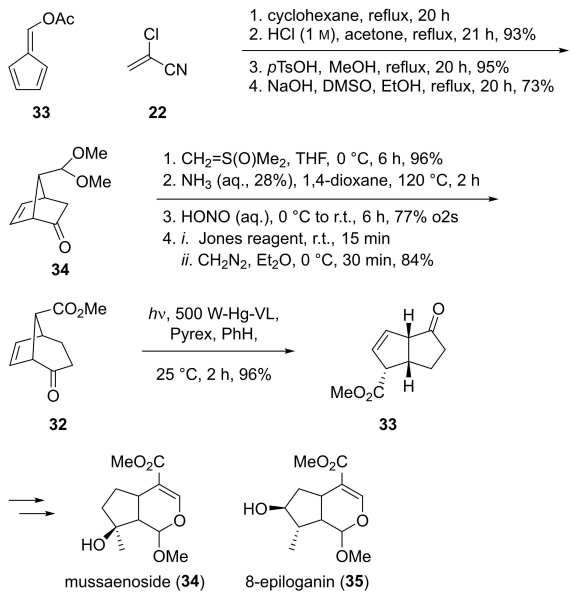


Scheme 5. Biosynthetic 1,3-acyl shift from **30** to calyculone D (**31**) observed by Fenical in 1991.[21] The diastereomer of **31** was also isolated but to impure to determine a yield. VL = vapor lamp.

Yamamoto and co-workers resumed Kato's route starting from anisole **25** to precursor **26** in their synthesis of capnellene (**27**). The 1,3-acyl shift from bridged **26** was performed in acetone (a triplet-sensitizer) and yielded fused **28** in 51% next to the product of the oxa-di-π-methane rearrangement **29** in 13% (Scheme 4).[20] An extensive screening of model substrates revealed that bulkier substituents hinder the 1,2-acyl shift sterically, thus formation of **29** is diminished.

In 1991, Fenical *et al.* reported the first biosynthetic 1,3-acyl shift in natural products as ring contraction from diterpenoid **30** to calyculone D (**31**) (Scheme 5); both isomers were isolated from the Caribbean gorgonian *Eunicea calyculata*.[21] Interestingly, pure **31** did not convert back to **30** upon irradiation with a 450 W high pressure mercury lamp for 8 h due to insufficient orbital overlap. Furthermore, *cis-trans* isomerization of both conjugated C–C double bonds in **30** was observed upon irradiation. Ring contractions from 8- to 5- and 7- to 5-membered rings based on 1,3-acyl shifts were elucidated earlier by Grider and Orito respectively.[22]

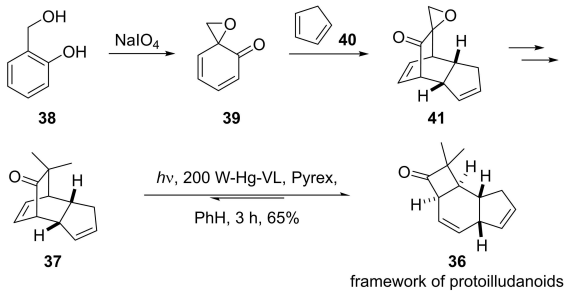
The so far highest yield of a 1,3-acyl shift was reported from Chang.[23] Their synthesis of precursor **32** commences again with a Diels–Alder reaction of 6-acetoxyfulvene **33** and α-chloroacrylonitrile **22**.[24] Hydrolysis of the enol acetate, acetal formation, and hydrolysis of the chloronitrile furnish ketone **34**.[24] A sequence of ring expansion and Jones oxidation is achieved in 62% over four steps to yield **32**.[23] The rearrangement of bridged **32** to its fused isomer **33**, the formal precursor of mussaenoside (**34**) and 8-epiloganin (**35**), proceeded in 96% yield (Scheme 6). We note that this almost quantitative shift of the photochemical equilibrium between **32** and **33** is unusual and that this is the only example reported in the literature in which an additional proximal carbonyl group is present in the molecule.



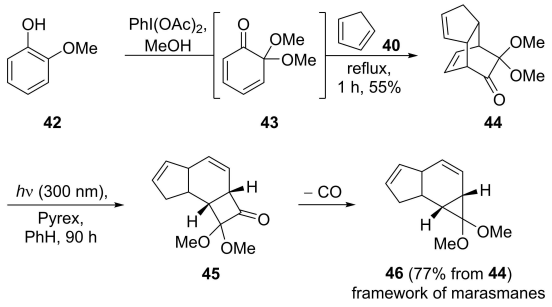
Scheme 6. Synthesis of mussaenoside (**34**) and 8-epiloganin (**35**) by Chang, 1993.[23]

The [4.6.5] ring system of protoilludanoids (**36**) was constructed by Singh and Porinchu with another 1,3-acyl shift from bridged **37** to fused **36** in 65% (Scheme 7).[25] Conversion of salicyl alcohol (**38**) with $NaIO_4$ to **39** and a subsequent *in situ* Diels-Alder reaction with cyclopentadiene **40** allowed access to epoxy ketone **41**.[25]

Moreover, Liao and co-workers utilized a [4+2] cycloaddition of a masked *o*-benzoquinone **43** and cyclopentadiene **40** again in 2010 to generate **44** (Scheme 8).[26] The rearrangement of **44** to **45** is accompanied by a subsequent irreversible decarbonylation of **45** to **46**. Upon further irradiation for 90 h the reaction system shifted to **46** in 77% which contains the carbon framework of marasmanes.



Scheme 7. Synthesis Singh's synthesis towards protoilludanoids (**36**).[25]



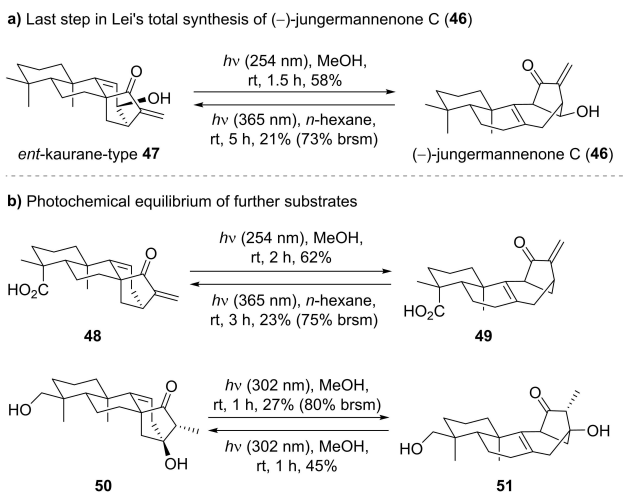
Scheme 8. Liao's synthesis towards marasmanes (**46**).[26]

An example for an equilibrium between a bridged β,γ-unsaturated ketone **46** and its spiro isomer **47** is presented in the final step of Lei's synthesis of (−)-jungermannenone C (**46**) (Scheme 9a).[13] The authors assume this step to be a spontaneous biosynthetic interconversion because *ent*-kaurane-type **47** and **46** interconvert into each other upon irradiation with sunlight. To expand the understanding of the photochemical equilibrium further substrates **48**–**51** were examined (Scheme 9b). In many cases several wavelengths were found to enable the interconversion and, in some cases, the optimal wavelengths were identical. Therefore, it was hard to correlate a wavelength with the optimal product distribution in general.

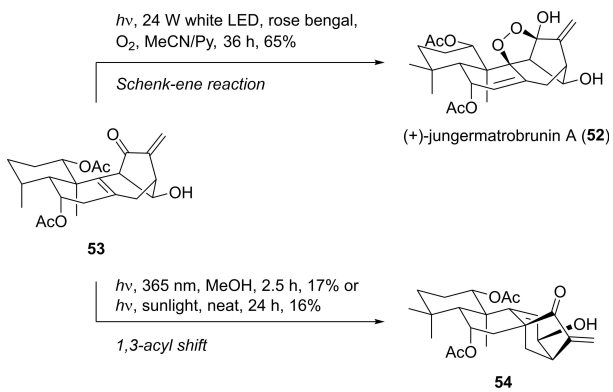
Also in 2019, Lei and co-workers observed a 1,3-acyl shift as an unexpected side reaction to a Schenck-ene reaction during the last step towards (+)-jungermatrobrunin A (**52**) (Scheme 10).[27] A detailed examination of this system revealed that the 1,3-acyl shift from **53** to **54** preceeds predominantly under UV irradiation whereas the desired Schenck-ene reaction of **53** to **52** is favored under visible light irradiation. Conclusively, both reactions may be biosynthetically possible as sunlight comprises UV and visible light and **52**, **53**, and **54** were isolated together.

The latest example for a 1,3-acyl shift as an elegant key step in total synthesis is contributed in our bioinspired synthesis of (−)-antroalbocin A (**55**) (Scheme 11).[28] Our synthesis features a photochemical domino process of deconjugation of 1,2-enone **56** and subsequent 1,3-acyl shift in the excited state from fused **57** to bridged **58**. The complete carbon backbone of **55** is already set in **56**, only the photochemical rearrangement of **56** constructs the bridged core structure in **58**. Immediate reduction in the dark of carbonyl C8 furnishes (−)-**55**.

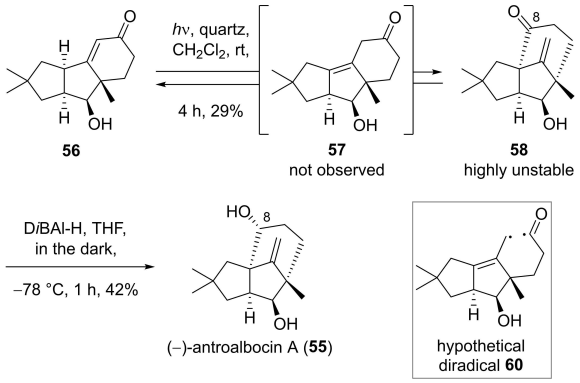
The comparison of the domino reaction (**56** to **58**, Scheme 11) to additional model substrates (Figure 3c) and a similar substrate by Paquette[11] (**15** to **16**, Figure 2 and Figure 3b) highlights the elevated yield of 29%. We hypothesized that the substituted cyclo-pentene core of **57** generates a



Scheme 9. a) Last step in Lei's synthesis of (−)-jungermannenone C (**46**);[13] b) examination of the photochemical equilibrium in further substrates **48**–**51**.[13] brsm = based on recovered starting material.

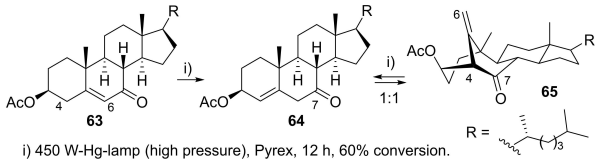


Scheme 10. Schenk-ene reaction under visible light irradiation in Lei's synthesis of (+)-jungermatrobrunin A (**52**) with an unexpected side reaction (1,3-acyl shift) from **53** to **54** under UV light irradiation.[27]



Scheme 11. Photochemical domino process in Kalesse's synthesis of (−)-antroalbocin A (**55**).[28] D*i*BAl-H = di-*iso*-butylaluminium hydride.

highly strained structure, which collapses immediately either to fused **56** or bridged **58**, hence, **57** was not detected in the reaction mixture. Consequently, the domino process was investigated computationally. The relative energies for species along the reaction sequence (in the ground state) is shown in Figure 3a. Most likely the solvent can assist the first two steps (**56** to **59** and **59** to **57**) leading to significantly decreased activation energies.[29] Thus, under the experimental conditions, the third step (1,3-acyl shift) might well be rate-determining. To demonstrate, that the 1,3-acyl shift proceeds in a concerted manner, we computed diradical **60** (Scheme 11) that would form upon homolytic bond cleavage in **57** and would then recombine to **58**. With 77.7 kcal mol^{-1} (with respect to **56**) it lies well above the reaction minima depicted in Figure 3a and can, therefore, not be important in the reaction sequence. Furthermore, the computed Gibbs free enthalpies ΔG_{298} of the 1,3-acyl shifts in Paquette's system[11] (**15** to **16**, Figure 3b) and our additional model substrates (**61** to **62**, Figure 3c) are all *endergonic*. This is in contrast to the last step in Figure 3a and



Scheme 12. Examination of photochemical rearrangement of 3β-acetoxy-cholest-5-en-7-one (**63**) by Nakanishi in 1969.[30]

probably the main reason for the lower yields in these reactions.

The general domino process of deconjugation and 1,3-acyl shift was already investigated thoroughly by Furutachi and Nakanishi in 1969 (Scheme 12).[30] Upon irradiation for 12 h a mutual exchange of C4 and C6 carbons in 3β-acetoxycholest-5-en-7-one (**63**) was observed. Deuteration at C6 and isolation of the deconjugated intermediate **64** substantiates that the skeletal rearrangement proceeds *via* photochemical deconjugation to **64** followed by a reversible 1,3-acyl shift to **65**.

4. Outlook and Conclusion

Photochemical, sigmatropic 1,3-acyl shifts are distinguished by (i) a stereospecific reaction mechanism, (ii) the tolerance of versatile protecting groups comprising also free alcohols, and (iii) their role in putative biosyntheses. Therefore, 1,3-acyl shifts can achieve the challenging construction of intricate carbon frameworks inherent in complex natural products elegantly. Yet, the decreased yields of the rearrangements of the fused isomer to its bridged counterpart appear unattractively. For cases in which the absorption maxima λ_{max} of the photochemically active isomers differ adequately, future studies comprising selective excitation with discrete wavelengths applying LASER or LED light sources may reinforce the enthusiasm of this

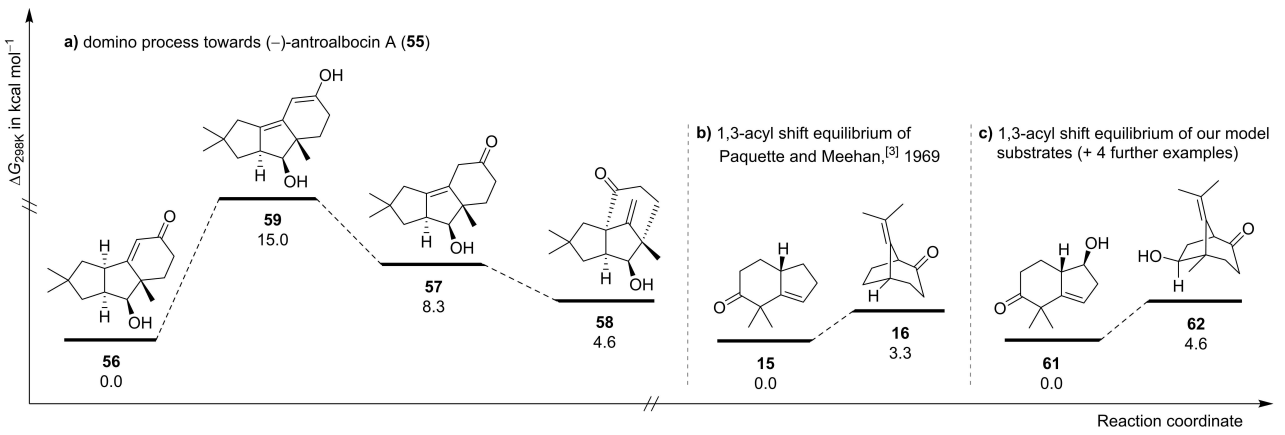


Figure 3. a) Relative energies for species along the reaction sequence of **56** to **58** computed at the PCM(CH_2Cl_2)-DLPNO-CCSD(T)/def2-QZVPP//PBEh-3c level of theory; b) Gibbs free enthalpies (at 298 K) of Paquette's[11] system **15** to **16**; and c) Gibbs free enthalpies of our model substrate **61** conversion to **62** computed at the same level of theory. Like Paquette's system (b) all reactions (c and further substrates) are endergonic, which is in contrast to the 1,3-acyl shift (a) in our total synthesis of (−)-antroalbocin A (**55**). Reprinted (adapted) with permission from *Organic Letters* **2022**, *24*, 5812–5816. Copyright 2022 American Chemical Society.

underrepresented transformation within the synthetic community.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: 1,3-Acyl shift · Natural products · Photochemistry · Terpenes · Total synthesis

[1] a) G. O. Schenck, R. Steinmetz, *Chem. Ber.* **1963**, *96*, 520–525; b) D. I. Schuster, M. Axelrod, J. Auerbach, *J. Tetrahedron Lett.* **1963**, 1911–1916.
[2] a) T. Gaich, P. S. Baran, *J. Org. Chem.* **2010**, *75*, 4657–4673; b) J. Schwan, M. Christmann, *Chem. Soc. Rev.* **2018**, *47*, 7985–7995.
[3] a) K. N. Houk, *Chem. Rev.* **1976**, *76*, 1–74; b) R. S. Givens, W. K. Chae, *J. Am. Chem. Soc.* **1978**, *100*, 6278–6280.
[4] R. G. W. Norrish, C. H. Bamford, *Nature* **1936**, *138*, 1016–1016.
[5] The review by N. Hoffmann contains a section on photochemical extrusion of small molecules. N. Hoffmann, *Chem. Rev.* **2008**, *108*, 1052–1103.
[6] The review by T. Bach, P. Hehn includes a section on Norrish-Yang cyclizations. T. Bach, P. Hehn, *Angew. Chem. Int. Ed.* **2011**, *50*, 1000–1045; *Angew. Chem.* **2011**, *123*, 1032–1077.
[7] R. G. W. Norrish, C. H. Bamford, *Nature* **1937**, *140*, 3535, 195–196.
[8] B. Reimann, D. E. Sandler, K. Schaffner, *J. Am. Chem. Soc.* **1986**, *108*, 5537–5530.
[9] P. S. Engel, M. A. Schexnayder, H. Ziffer, J. I. Seeman, *J. Am. Chem. Soc.* **1974**, *96*, 924–925.
[10] S. Wilsey, M. J. Bearpark, F. Bernardi, M. Olivucci, M. A. Robb, *J. Am. Chem. Soc.* **1996**, *118*, 176–184.
[11] L. A. Paquette, G. V. Meehan, *J. Org. Chem.* **1969**, *34*, 450–454.
[12] W. F. Erman, H. C. Kretschmar, *J. Am. Chem. Soc.* **1967**, *89*, 3842–3846.
[13] B. Hong, W. Liu, J. Wang, J. Wu, Y. Kadonaga, P.-J. Cai, H. X. Lou, Z.-X. Yu, H. Li, X. Lei, *Chem.* **2019**, *5*, 1671–1681.
[14] a) R. C. Cookson, N. S. Wariyar, *J. Chem. Soc.* **1956**, 2302; b) H. Labhart, G. Wagniere, *Helv. Chim. Acta* **1959**, *42*, 2219–2227; c) G. Büchi, E. M. Burgess, *J. Am. Chem. Soc.* **1960**, *82*, 4333–4337; d) J. S. Swenton, *J. Chem. Educ.* **1969**, *46*, 217–226.
[15] a) M. Büschleb, S. Dorich, S. Hanessian, D. Tao, K. B. Schenthal, L. E. Overman, *Angew. Chem. Int. Ed.* **2016**, *55*, 4156–4186; *Angew. Chem.* **2016**, *128*, 4226–4258; b) F. Schneider, K. Samarin, S. Zanella, T. Gaich, *Science* **2020**, *367*, 6478, 676–681.
[16] Transmission range of vycor glass (>220–230 nm) and Pyrex glass (>290–300 nm). M. T. Crimmins, T. L. Reinhold, *Enone olefin [2+2] photochemical cycloadditions, Organic Reactions* **2004**, *44*, 297–588.
[17] a) T. Uyehara, Y. Kabasawa, T. Kato, T. Furuta, *Tetrahedron Lett.* **1985**, *26*, 2343–2346; b) T. Uyehara, Y. Kabasawa, T. Kato, *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2521–2528.
[18] This transformation presumably proceeds through a thioketone which is hydrolysed *in situ*. D. A. Evans, W. L. Scott, L. K. Truesdale, *Tetrahedron Lett.* **1972**, *13*, 121–124.
[19] a) T. Uyehara, T. Furuta, Y. Kabasawa, J. I. Yamada, T. Kato, *J. Chem. Soc. Chem. Commun.* **1986**, *7*, 539–540; b) T. Uyehara, T. Furuta, Y. Kabawawa, J. I. Yamada, T. Kato, Y. Yamamoto, *J. Org. Chem.* **1988**, *53*, 3669–3673.
[20] T. Uyehara, T. Furuta, M. Akamatsu, T. Kato, Y. Yamamoto, *J. Org. Chem.* **1989**, *54*, 5411–5413.
[21] J. Shin, W. Fenical, *J. Org. Chem.* **1991**, *56*, 1227–1233.
[22] a) K. G. Hancock, R. O. Grider, *J. Am. Chem. Soc.* **1974**, *96*, 1158–1168; b) H. Suginome, T. Ohtsuka, Y. Yamamoto, K. Orito, C. Jaime, E. Osawa, *J. Chem. Soc, Perkin Transactions* **1990**, *1*, 1247–1253.
[23] L.-F. Hsu, C.-P. Chang, M.-C. Li, N.-C. Chang, *J. Org. Chem.* **1993**, *58*, 4756–4757.
[24] a) E. D. Brown, R. C. Clarkson, T. J. Leeney, G. E. Robinson, *J. Chem. Soc. Perkin Trans. 1* **1978**, 1507–1511; b) N.-C. Chang, W.-F. Lu, C.-Y. Tseng, *J. Chem. Soc. Chem. Commun.* **1988**, 182–183.
[25] V. Singh, M. Porinchu, *J. Chem. Soc. Chem. Commun.* **1993**, *2*, 134–136.
[26] D.-S. Hsu, Y.-Y. Chou, Y.-S. Tung, C.-C. Liao, *Chem. Eur. J.* **2010**, *16*, 3121–3131.
[27] J. Wu, Y. Kadonaga, B. Hong, J. Wang, X. Lei, *Angew. Chem. Int. Ed.* **2019**, *58*, 10879–10883; *Angew. Chem.* **2019**, *131*, 10995–10999.
[28] B. Siekmeyer, D. Lübken, K. Bajerke, B. Bernhardt, P. R. Schreiner, M. Kalesse, *Org. Lett.* **2022**, *24*, 5812–5816.
[29] Y. Valadbeigi, H. Farrokhpour, *Int. J. Quantum Chem.* **2013**, *113*, 2372–2378.
[30] N. Furutachi, Y. Nakadaira, K. Nakanishi, *J. Am. Chem. Soc.* **1969**, *91*, 1028–1030.

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