156. Cascade Cyclizations of Terpenoid Polyalkenes Triggered by Photoelectron Transfer – Biomimetics with Photons[1][2]

by **Klaus-Dieter Warzecha, Xuechao Xing,** and **Martin Demuth***

Max-Planck-Institut für Strahlenchemie, D-45413 Mülheim an der Ruhr

and **Richard Goddard, Magnus Kessler,** and **Carl Krüger**[3]

Max-Planck-Institut für Kohlenforschung, D-45466 Mülheim an der Ruhr

(31.VII.95)

Light-induced cyclizations of suitably functionalized polyalkene terpenoids, such as geranyl, all-*trans*-farnesyl, and all-*trans*-geranylgeranyl derivatives, *via* formation of radical cations are proven to be a powerful method for the single-step synthesis of mono- and mostly all-*trans*-fused polycyclic compounds from readily available precursors. Whereas some of these highly stereo- and chemoselective transformations required the use of micellar media, they can now be conveniently performed in homogeneous solutions upon suitable choice of the electron acceptors and of the functionality pattern of the polyalkene substrates. Moreover, the mode of cyclization, *i.e.*, 6- *vs.* 5-membered ring formation and termination of the cyclization cascades, are steered efficiently by the substituents of the polyalkenes (polyalkenyl acetate *vs.* α,β-unsaturated ethyl polyalkenoate and polyalkene-1,1-dicarbonitrile). At the same time, the protic solvents used add highly stereoselectively to the ω-alkene sites of the polyalkens in *anti-Markovnikov* sense which strongly suggests that radical cations are intercepted. Interestingly, the transformations achieved here upon photoelectron transfer parallel the biosynthetic paths of non-oxidative terpene cyclizations which are thought to occur purely by protonation of the isoprenoid polyalkenes.

Introduction. – Previously, we showed using a series of isoprenoid polyalkenes, such as the acetates **1** of geraniol ($R^1 = H$, $R^2 = AcOCH_2$), **7** of all-*trans*-farnesol ($R^1 = H$, $R^2 = AcOCH_2$), and **11a** of all-*trans*-geranylgeraniol (**11a**) [1] that photochemically induced electron transfer (PET) [2] affords exclusively 6-membered and *trans*-fused cyclic products **2** (*Scheme 1*), **8** (*Scheme 2*), and **12a** (*Scheme 3*), respectively. In the course of these reactions, H_2O adds highly stereoselectively as a nucleophile in *anti-Markovnikov* sense to the ω-alkene of the polyalkene substrates upon PET. The *anti-Markovnikov* addition of a protic solvent strongly suggests that radical cations [3] are intercepted [4]. These transformations were best performed in the presence of benzene-1,4-dicarbonitrile together with phenanthrene as an electron-acceptor couple and in micellar media, since in homogeneous solutions *cis/trans*-isomerization predominated. These experiments did not reveal whether the detergent, *viz.* sodium dodecyl sulfate (SDS) used preferably in that work, was necessary as mediator for *a*) the proper folding

[1] Presented in part at the '10th International Conference on Organic Synthesis (IUPAC-ICOS 10)', 11–16 December, 1994, Bangalore, India, and at the 'IUPAC-POST ICOS 10 Symposium', 19–20 December, 1994, Trivandrum, India. For earlier work in this series, see [1].

[2] This paper is dedicated to Prof. *Hans-Dieter Scharf*, RWTH Aachen, on the occasion of his 65th birthday.

[3] Elucidation of X-ray structures by *R. G.*, *M. K.*, and *C. K.*

of the polyalkenes prior to cyclization and/or *b*) an enhanced separation and hence longer lifetimes of the intermediate radical ion pairs enabling the attempted bond forming reaction cascade.

Results and Discussion. – 1. *Cyclizations and Reaction Conditions.* In contrast to the above mentioned earlier findings where the use of micellar medium, *i.e.*, SDS in H_2O, was crucial for the transformations of the polyalkenyl acetates **1**, **7** (R^1 = H, R^2 = $AcOCH_2$), and **11a** to the 6-membered cyclic products **2**, **8**, and **12a** [1], respectively, we recently found that these cyclizations proceed also in homogeneous media upon proper choice of the reaction conditions [5]. Best results are achieved, if 2,3,5,6-tetramethylbenzene-1,4-dicarbonitrile is employed in combination with 1,1′-biphenyl as the electron-acceptor couple and under 300-nm irradiation in MeCN/H_2O 4:1 or MeCN/MeOH 4:1 affording the photoproducts in at least 15–30% yields[4]) depending on the substrates used. The advantageous use of this particular acceptor combination was previously demonstrated and discussed in more detail in connection with a PET-triggered lactonization [6]. Bulky substituents at the CN-substituted aromatic acceptors seem to be important for efficient suppression of electron back-transfer.

On average, even higher yields, together with a synthetically intriguing change of the mode of cyclization, are encountered in case of the PET-triggered reactions of polyalkene derivatives containing electron-withdrawing functional groups instead of the allyl acetate moiety, in homogeneous solution (300-nm irradiation in MeCN/H_2O 4:1 or MeCN/MeOH 4:1) [5] [7]. Thus, the α,β-unsaturated 1,1-dicarbonitriles **1**, **7** (R^1 = R^2 = CN), and **11c** cyclize characteristically to 5-membered (**3**[5]) and **5**, 55% yield), 6/5-membered (**9** and **10**[6]), 25–30% yield), and 6/6/5-membered (**13c**, 25% yield) cyclic photoproducts. As will be seen later, the 5-membered rings are likely to be the result of the respective termination step of the individual cyclization cascades. The α,β-unsaturated ethyl polyalkenoate **11b**, on the other hand, yields a 65:35 mixture of the 6/6/6- and 6/6/5-membered tricyclic compounds **12b** and **13b**. Whereas **13b** is a single diastereoisomer (3β-methyl isomer), **12b** is a 1:3 mixture of the 1α- and 1β-isomers which were so far not separable either by medium-pressure column chromatography (silica gel) or by HPLC[7])[8]).

Notably, all of these transformations can be performed in homogeneous media, *i.e.*, in MeCN/H_2O or MeCN/MeOH[9]) solutions, irrespective of the choice of the electron-

---

[4]) Yields refer to chromatographically (medium-pressure silica-gel columns) isolated and > 96% pure compounds.

[5]) Since the isomers of **3** could not be separated chromatographically, the 1:1 mixture of the photoproducts was acetylated to afford a chromatographically separable mixture of **4** (see *Exper. Part*).

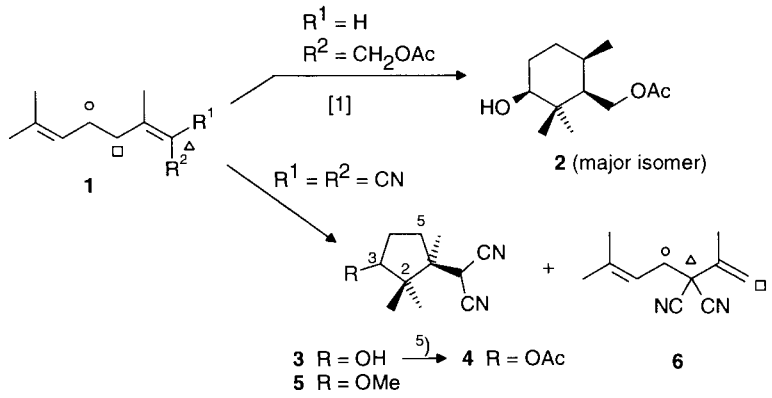
[6]) **Footnote added in proof:** Structure **10** has also been confirmed by X-ray analysis.

[7]) For unambiguous structure assignment, the mixture of **12b** was silylated ((*t*-Bu)Me_2SiCl) at OH–C(7), and the ester function reduced to the alcohol. The resulting 1:3 diastereoisomer mixture was then compared spectroscopically with a parent stereoisomer mixture which was obtained in two steps from the known 1-epimers **12a** [1] by silylation at OH–C(7) followed by selective saponification of the acetates to the primary alcohols [5].

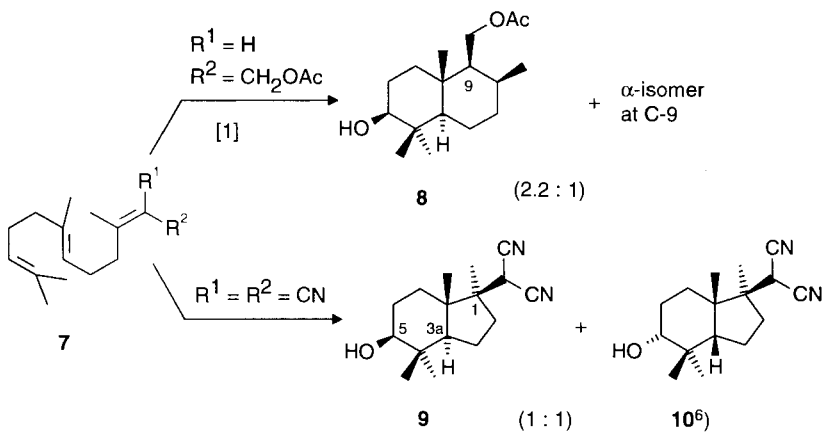
[8]) The α/β terminology used in this paper is adopted from the steroid convention, *i.e.*, α means below and β above the paper plane.

[9]) Preliminary experiments revealed that in analogy to the transformation **1** → **5** described in this paper, cyclizations with **7** and **11** can also be achieved when MeOH instead of H_2O is added to C(3) of the respective bi- and tricyclic products.

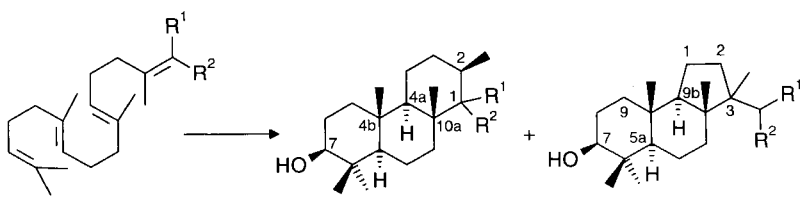
Scheme 1[8])



Scheme 2[8])



Scheme 3[8])



a	R^1 = H, R^2 = CH_2OAc	100[a])	: 0
b	R^1 = H, R^2 = CO_2Et	65[b])	: 35 (3β-methyl)
c	R^1 = R^2 = CN	0	: 100 (3α-methyl)

[a]) 1α/1β epimers 1:3.8 [1]. [b]) 1α/1β epimers 1:3.

acceptor couple. However, the electron-acceptor combinations influence markedly the cyclization efficiency as well as the product yields. Generally lower yields of cyclic products result, if naphthalene-1-carbonitrile or a combination of 1,1′-biphenyl and benzene-1,4-dicarbonitrile are used as the electron acceptors ($\lambda_{irr.}$ 300 nm, *Pyrex* glass; yields 2–6%), and if the acceptor couple phenanthrene/benzene-1,4-dicarbonitrile is employed under 350-nm irradiation (yields 8–25%) [1]. We now found that significantly higher product yields of 25–55% are achieved, if the reactions are run with 1,1′-biphenyl/2,3,5,6-tetramethylbenzene-1,4-dicarbonitrile as the electron-acceptor combination at $\lambda_{irr.}$ 300 nm (*Pyrex* glass, 12–15 h, 2–4%*w*/*w* samples). Very sluggish and incomplete transformations are encountered in this series with phenanthrene/2,3,5,6-tetramethylbenzene-1,4-dicarbonitrile ($\lambda_{irr.}$ 350 nm).

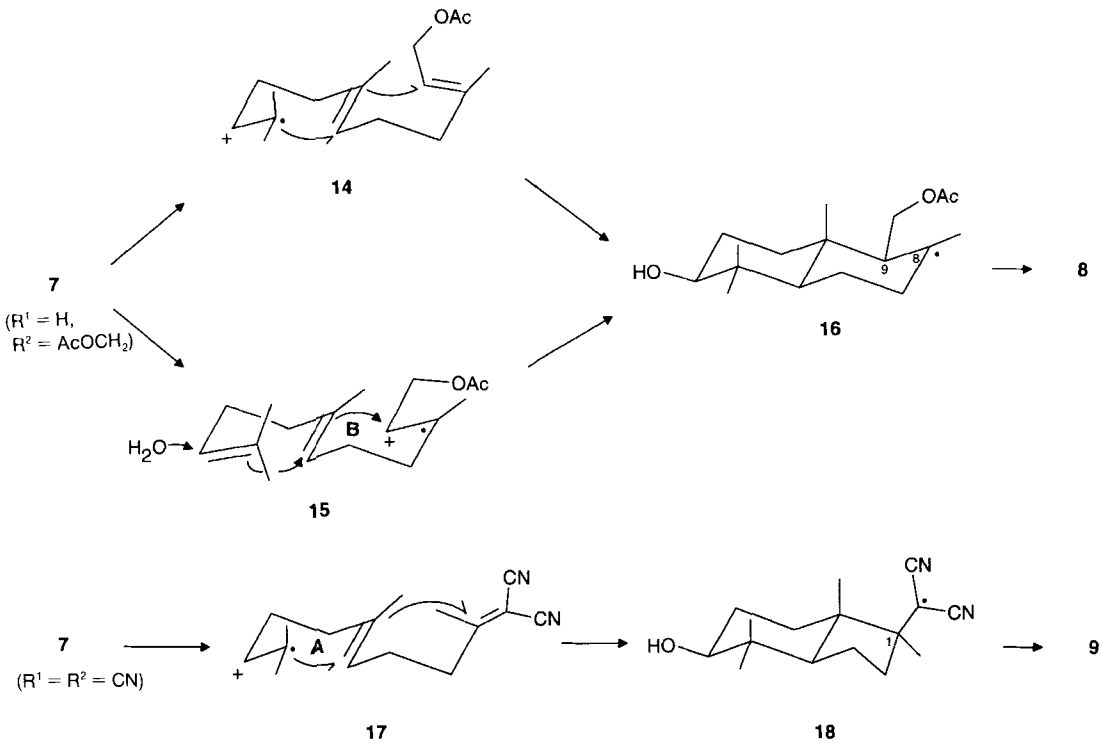
In contrast to the electron-acceptor pairs earlier employed, which were composed of naphthalene-1-carbonitrile or benzene-1,4-dicarbonitrile, the combination with 2,3,5,6-tetramethylbenzene-1,4-dicarbonitrile is sufficiently reactive even in catalytic amounts of 0.1–0.2 mol-equiv. without noticeable decomposition of the acceptors. This result parallels the earlier findings on the previously mentioned lactonization [6].

In this context it is also important to note that it is advantageous to use *Pyrex* filters or vessels for the irradiations at 300 nm. Thus, the formation of major amounts of by-products resulting from direct light absorption by **1** is avoided. One major by-product of the transformation of **1** ($R^1 = R^2 = CN$) was successfully isolated and characterized to be **6**. Mechanistically this material is likely to arise from cleavage of the central bond of **1** (□,o) to give a pair of allylic radicals which ultimately recombines at the C-atoms △,o, in analogy to the known photochemical cleavage and rearrangement of 3,7-dimethylocta-2,6-diene-1-nitrile upon direct excitation with 254-nm light [8]. For unambiguous structure assignment of **6**, this material was prepared in larger quantities in yields of 50–60% by irradiation of **1** ($R^1 = R^2 = CN$) in MeCN without electron-acceptor additives at 300 nm and in a quartz vessel.

2. *Mechanistic Reflections on the Cyclization Processes.* 2.1. *General.* Two main categories of cyclization modes are operative, the first of which comprises all-6-*endo-trig* bond formation and the second involves a 5-*exo-trig* process combined with the formation of zero to two 6-membered rings depending on the size of the polyalkene starting materials. Whereas the transformations of the polyalkenyl acetates fall into the first category (see *2.2*), the α,β-unsaturated polyalkene-1,1-dicarbonitriles follow exclusively the second option, and mixed reactivity is encountered for the cyclization of an α,β-unsaturated polyalkenoate (see *2.3*). Notably, for these two types of polyalkenes, it is anticipated that the α,β-unsaturation sites will not be oxidized primarily because of their elevated oxidation potentials as compared to the trialkyl-substituted alkenes in the respective substrates.

2.2. *Polyalkenyl Acetates.* The products of the allyl acetates could either be derived from free-radical-type (*via* **14** → **16**) or ionic (*via* **15** → **16**) all-chair cyclizations as exemplified in *Scheme 4* for the transformation of all-*trans*-farnesyl acetate (**7**; $R^1 = H$, $R^2 = AcOCH_2$) to **8**. The corresponding chair/boat folding would accordingly lead to the 9α-isomer of **8**. An important question concerns scavenging of the free-radical site which develops at C(8) of **16** in the course of such a sequential bond-forming cascade in either mechanistic route from **14** or **15**. Potentially, three mechanisms for the termination step, *i.e.*, saturation at C(8) of **16** *en route* to **8**, are conceivable: *a*) disproportionation,

Scheme 4. *Mechanistic Reflections on the Cyclization Cascades of* **14** *and* **15** *to* **8** via **16** (6-*endo-trig* mode), *and of* **17** *to* **9** via **18** (5-*exo-trig* mode). Two reaction paths are not shown: *a*) The alternate pseudo-chair ring B conformation of **15**, leading to the C(9)-epimer of **16**, and *b*) the alternate pseudo-chair ring A conformation of **17**, leading to **10**.



b) reduction of the C(8) radical by the [acceptor]$^{\cdot-}$[10]) to form an anion at C(8) prior to protonation, and *c*) H-abstraction by the C(8) radical, which would likely involve abstraction of an allylic H-atom from unreacted **7**. The first option applies to a very minor reaction path, since only marginal amounts of olefinic cyclization products could be detected [5]. The second alternative is very unlikely in view of the anticipated endothermicity of the reduction of the C(8) radical to the corresponding anion (*cf.* [9] and refs. 11, 20 therein: $E^{red}_{1/2}$ for *tert*-butyl radical −2.0/−2.54 V *vs.* SCE). Therefore, H-abstraction from unreacted polyalkene or MeCN could be a favorable mechanism for the termination step in this series of compounds.

As in the previous experiments using SDS, the solvent adds in homogeneous solution cleanly in *anti-Markovnikov* sense to the alkene which is again in accord with a radical-cation mechanism. In addition, this process is in all examples highly stereo- and chemoselective, *i.e.*, interception occurs equatorially and exclusively at the ω-alkene of the starting polyalkenes.

---

[10]) This species is assumed to be the radical anion of 2,3,5,6-tetramethylbenzene-1,4-dicarbonitrile formed upon reduction of electronically excited 2,3,5,6-tetramethylbenzene-1,4-dicarbonitrile by 1,1′-biphenyl which in turn forms a radical cation being the oxidant of the alkene [6].

2.3. *α,β-Unsaturated Polyalkene-1,1-dicarbonitriles and Ethyl Polyalkenoates.* In contrast to the reactions of the polyalkenyl acetates (see *2.2*), the analogous α,β-unsaturated 1,1-dicarbonitriles undergo cyclizations to 5-membered (**3** and **5**), 6/5-membered (**9** and **10**), and 6/6/5-membered (**13c**) ring photoproducts. The characteristic formation of a 5-membered ring in each of these examples is a likely result of favorable radical stabilization as exemplified for **7** → **9** *via* **17** and **18** in *Scheme 4*. The malonodinitrile radical intermediate **18**, resulting from a 5-*exo-trig* cyclization, should be stabilized by *ca.* 8.5 kcal·mol^{-1} [10] as compared with the alternative trialkyl-substituted radical transient which would result from a 6-*endo-trig* closure in analogy to **16**. We ascribe the stereochemical outcome of this process with regard to C(1) to least steric interaction of the malonodinitrile residue with the *pro*-angular Me group in the transition state *en route* to the 5-membered ring. Similar reasoning should also apply to the other examples.

A lower selectivity is observed, however, for the transformation of the α,β-unsaturated ethyl polyalkenoate **11b** which affords a mixture of 6/6/6- and 6/6/5-membered photoproducts (**12b** and **13b**). Again, this result can be rationalized by the argument of transient-radical stabilization, *i.e.*, of the radicals at C(1) of **12b** *vs.* $^{\cdot}CH_2COOEt$ of **13b**. The stabilizing power of the ester group should lie between the one of a trialkyl and of a dicarbonitrile moiety [10]. Therefore, the 6-*endo- vs.* 5-*exo-trig* selectivity of the terminal ring closure is clearly expected to be less pronounced than in the polyalkenyl acetate and polyalkene dicarbonitrile transformations.

The question concerning scavenging of the free-radical site which develops in the course of the cyclization process was also addressed for the case of the dicarbonitriles. A reaction with **1** ($R^1 = R^2 = CN$), carried out in D_2O/MeCN, gave very cleanly photoproduct **3** deuteriated in α-position to the two CN groups (> 98% deuteriation) suggesting reduction of the intermediate radical in α-position by the radical anion of 2,3,5,6-tetramethylbenzene-1,4-dicarbonitrile followed by deuteration. This mechanistic variant, as compared to the polyalkenyl acetate reactivity, is readily understandable in view of the considerable radical and anion stabilization by the CN groups.

3. *X-Ray Analyses.* In addition to the routine extensive spectroscopic analyses, the structures of **2** and **9** were secured by X-ray analyses (see *Table*, *Fig.*, and supplementary material). Colorless cubes of **2** and **9** were obtained upon repeated crystallizations from pentane/acetone and pentane/Et_2O, respectively. The X-ray data were collected under Ar at room temperature on an *Enraf-Nonius-CAD-4* diffractometer. The structures were solved by direct methods using the SHELXS-86 program with subsequent full-matrix least-squares refinement (SHELX-93). Atomic coordinates, anisotropic thermal parameters, bond lengths, and angles, torsion angles, and structural factors were deposited as supplementary material. The crystal data and selected parameters of the data collection are listed in the *Table*. Some special features of the structure of **9** are worth mentioning. The perhydroindane **9** crystallizes as a conglomerate [11] in the chiral space group $P2_12_12_1$ with parallel helical chains of molecules separated by distances greater than the sum of the respective *van der Waals* radii. In each chain, molecules are linked by intermolecular H-bonds between the OH group of one molecule and one CN group of its neighbor (O···N 2.963(2) Å; see *Fig.*). This type of packing implies that the crystallization process is enantioselective. In view of its potential for the synthesis of enantiomerically pure compounds, this chiral crystal growth is under further investigation.

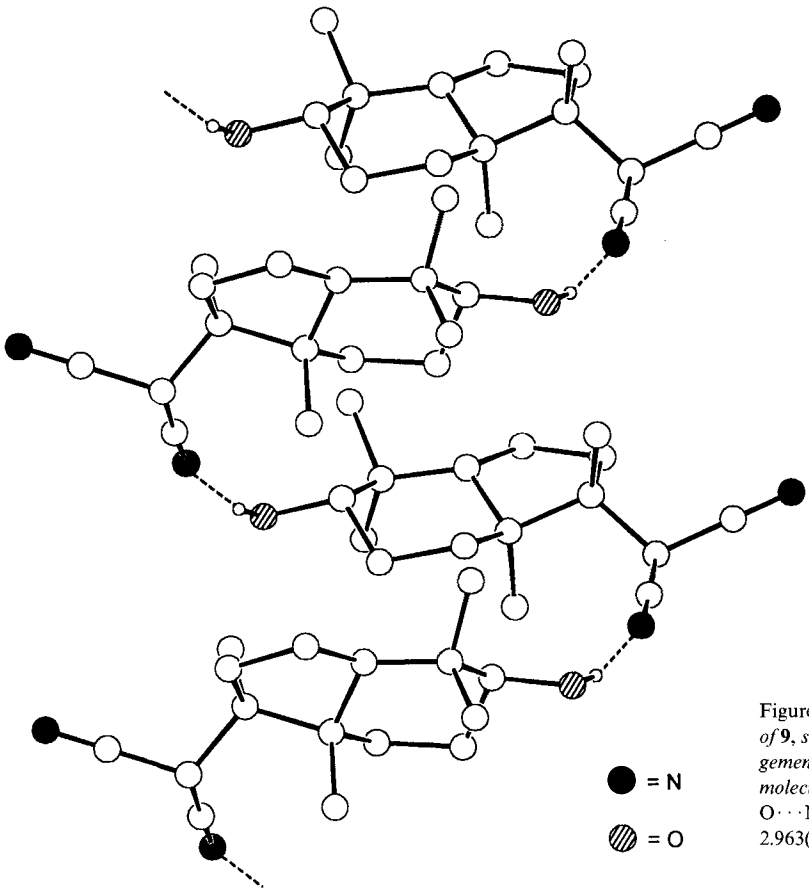


Figure. *X-Ray structure of* **9**, *showing the arrangement of H-bonded molecules in the crystal.* O···N distance 2.963(2) Å (dashed).

Table. *Crystal Data and Parameters for* **2** *and* **9**

	2	**9**		**2**	**9**
Molecular formula	$C_{12}H_{22}O_3$	$C_{16}H_{24}N_2O$	μ [cm^{-1}]	0.77	5.34
Crystal size [mm]	$0.25 \times 0.39 \times 0.39$	$0.14 \times 0.18 \times 0.67$	Measured reflections	2913	3255
Crystal system	triclinic	orthorhombic	h	$-10 \rightarrow 10$	$-9 \rightarrow 9$
Space group	$P\bar{1}$ (No. 2)	$P2_12_12_1$ (No. 19)	k	$-11 \rightarrow 11$	$0 \rightarrow 18$
a [Å]	7.443(1)	6.733(1)	l	$0 \rightarrow 14$	$0 \rightarrow 24$
b [Å]	8.321(1)	13.702(1)	Independent reflections	2760	3023
c [Å]	10.560(1)	16.128(2)	Observed reflections	2101	2779
α [°]	69.14(1)	90		$[I \geq 2\sigma(I)]$	$[I \geq 2\sigma(I)]$
β [°]	84.42(1)	90	Refined parameters	224	268
γ [°]	83.25(1)	90	$(\sin\theta/\lambda)_{max}$ [Å^{-1}]	0.65	0.63
V [Å^3]	605.8(1)	1488.0(2)	R_{int}	0.01	0.01
Z	2	4	θ_{max}	27.45°	75.00°
D_{calc} [g·cm^{-3}]	1.17	1.16	$(\Delta/\sigma)_{max}$	1.24	0.04
K_α Radiation	Mo	Cu	$\Delta\rho_{max}$ [e Å^{-3}]	0.35	0.26
Wavelength [Å]	0.71069	1.54178	R	0.065	0.038
Scan method	$\omega/2\theta$	$\omega/2\theta$	R_w ($\omega = 1/\sigma^2(F_o)$)	0.084	0.046

4. *Conclusion.* The transformations described in this paper represent a powerful (photo)synthetic method for a single-step build-up of arrays of stereogenic centers, *e.g.* up to seven in case of the formation of **12a,b**, from readily accessible starting materials. Furthermore, the need of only catalytic amounts of the electron-acceptor couple and the possibility of performing most of these cyclizations in homogeneous solutions rather than in microheterogeneous media, thus avoiding laborious workup procedures, considerably augment the synthetic utility of this methodology. The role of SDS in such experiments – if required at all – is obviously not the one of a mediator for the proper folding of the substrates but rather for enhanced ion-pair separation, so inhibiting electron back-transfer, and thus promoting the cyclization processes even with electron acceptors of little steric bulk. A search for even more suitable electron-acceptor couples together with more detailed investigations on the termination step(s) might lead to still further improvement of preparative applications of these types of cyclization cascades. No statement can be made at this point on the sequence of the two main mechanistic events, the solvent addition to the radical cation site of the polyalkene and the cyclization process itself.

In addition, the transformations reported here constitute the first examples of photochemical terpene cyclizations *via* radical cations, which resemble strongly the parent classical non-oxidative biosynthetic processes [12]. These are thought to occur, in analogy to the parent oxidative mechanisms[11]), purely by protonation of the isoprenoid polyalkene substrates *via* carbenium-ion intermediates leading to all-*trans*-fused polycyclic products with stereoselective *anti-Markovnikov*-type incorporation of H_2O.

The continuous encouraging support of this work by Prof. *K. Schaffner* and financial support by the *Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen* are gratefully acknowledged.

Experimental Part

General. GLC: *Carlo-Erba-4100* and *Hewlett-Packard-427* instruments equipped with 25-m *OV-1* and 10-m *OV-1* glass capillary columns, resp. HPLC: *Merck-Hitachi-L-6000* gradient system coupled to a *Knauer* differential refractometer and coupled to a computing system; column: 250 × 8 mm, silica gel *100* (7 μm); gradient: cyclohexane/*tert*-butyl methyl ether. Melting points (m.p.): *Kofler* hot stage; uncorrected. UV/VIS Spectra: in MeCN; *Bruins* (Munich) *Omega-10* spectrophotometer; $\lambda_{max}(\varepsilon)$ in nm. IR Spectra (cm^{-1}): KBr pellets; *Perkin-Elmer-580* instrument. ^{13}C- (100.6 and 67.9 MHz) and ^1H-NMR Spectra: in $CDCl_3$; *Bruker-AM-400* and *-WH-270* instruments; chemical shifts δ in ppm; NOE enhancements are not mentioned if found between geminal or strongly coupled vicinal protons; abbreviations: *s* (strong), *m* (medium), *w* (weak). Electron impact (EI) MS: *Finnigan-MAT-8200* instrument using 70 eV electrons; *m/z* (rel. %).

Electron Acceptors and Starting Materials. Phenanthrene and 1,1′-biphenyl were purchased from *Fluka AG*. The 2,3,5,6-tetramethylbenzene-1,4-dicarbonitrile was prepared from 2,3,5,6-tetramethylbenzene *via* 1,4-diiodo-2,3,5,6-tetramethylbenzene according to [14], followed by 1,4-dicyanation of according to [15], but using DMF instead of HMPT [16]. Geranyl acetate and all-*trans*-farnesyl acetate (**1** and **7**, resp.; $R^1 = H$, $R^2 = AcOCH_2$) were purchased from *Aldrich*. all-*trans*-Geranylgeranyl acetate (**11a**) was prepared according to [17] from all-*trans*-geranylgeraniol [18]. Ethyl geranylgeranoate (**11b** as a 10:1 (2*E*)/(2*Z*)-mixture) was prepared following the procedure in [18]; for spectroscopic data, see [17a].

1,1-Dicarbonitriles **1**, **7**, *and* **11c** *by* Knoevenagel *Condensations.*

General Procedure. Under Ar, 100 mmol of 6-methylhept-5-en-2-one (→ **1**), geranylacetone (→ **7**), or all-*trans*-farnesylacetone (→ **11c**) and 10.5 g (160 mmol) of freshly distilled malonodinitrile, piperidine (6 ml),

[11]) The original concept involving *cationic* intermediates in oxidative cyclizations was set forth by *Eschenmoser et al.* [13a] and *Stork* and *Burgstahler* [13b].

AcOH (3 ml), and H_2O free $CaSO_4$ (35 g) were stirred in CH_2Cl_2 (500 ml) for 24 h at r.t. The mixture was then filtered through kieselguhr and the residue carefully washed with Et_2O (500 ml). The combined org. extract was washed with H_2O (6 ×) and brine (1 ×), dried (Na_2SO_4), and evaporated and the brownish viscous oily residue chromatographed (800 g of silica gel *Merck 60*; medium-pressure *Lobar* column, 0.040–0.063 mm; pentane/Et_2O 30:1 → 5:1). The 1,1-dicarbonitriles **1**, **7**, and **11c** were isolated in 81–91% yield as yellowish oils in > 95% purity.

2,6-Dimethylhepta-1,5-diene-1,1-dicarbonitrile (**1**; $R^1 = R^2 = CN$). UV: 226 (10467), 312 (101). IR: 2972*s*, 2917*s*, 2861*s*, 2232*s*, 1598*s*, 1451*s*, 1378*s*, 820*m*. ^{1}H-NMR (^{1}H,^{1}H-COSY, 270 MHz): 5.03 (*mt*, H–C(5)); 2.57 (*t*, 2 H–C(3)); 2.29–2.20 (*m*, 2 H–C(4)); 2.23 (*s*, Me–C(2)); 1.67 (*d*, 3 H–C(7)); 1.59 (*s*, Me–C(6)). ^{13}C-NMR (BB, DEPT, ^{13}C,^{1}H-COSY, 67.9 MHz): 181.84 (C(2)); 134.91 (C(6)); 120.52 (C(5)); 111.83 (CN); 111.61 (CN); 85.98 (C(1)); 37.88 (C(3)); 26.05 (C(4)); 25.49 (C(7)); 22.45 (*Me*–C(2)); 17.52 (*Me*–C(6)). MS: 174 (2, M^+, $C_{11}H_{14}N_2^+$), 69 (100), 41 (57), 39 (16), 27 (10).

(5E)-2,6,10-Trimethylundeca-1,5,9-triene-1,1-dicarbonitrile (**7**; $R^1 = R^2 = CN$). UV: 226 (11982), 312 (126). IR: 2968*s*, 2919*s*, 2858*s*, 2232*s*, 1599*s*, 1449*s*, 1377*s*, 832*m*. ^{1}H-NMR (^{1}H,^{1}H-COSY, 400 MHz): 5.04 (*mt*, H–C(9), H–C(5)); 2.58 (*t*, 2 H–C(3)); 2.29–2.22 (*m*, 2 H–C(4)); 2.23 (*s*, Me–C(2)); 2.06–2.01 (*m*, 2 H–C(8)); 1.64 (*s*, 3 H–C(11)); 1.58 (*s*, Me–C(10)); 1.57 (*s*, Me–C(6)). ^{13}C-NMR (BB, DEPT, ^{13}C,^{1}H-COSY, 100.6 MHz): 181.32 (C(2)); 138.48 (C(6)); 131.51 (C(10)); 123.73 (C(9)); 120.35 (C(5)); 111.78 (CN); 111.61 (CN); 85.94 (C(1)); 39.41 (C(7)); 37.82 (C(3)); 26.30 (C(8)); 25.94 (C(4)); 25.51 (C(11)); 22.43 (*Me*–C(2)); 17.51 (*Me*–C(10)); 15.87 (*Me*–C(6)). MS: 242 (2, M^+, $C_{16}H_{22}N_2^+$), 199 (5), 137 (3), 81 (7), 69 (100), 41 (34).

(5E,9E)-2,6,10,14-Tetramethylpentadeca-1,5,9,13-tetraene-1,1-dicarbonitrile (**11c**; $R^1 = R^2 = CN$). UV: 226 (10532), 312 (44). IR: 2967*s*, 2919*s*, 2856*s*, 2232*s*, 1599*s*, 1449*s*, 1377*s*, 1107*w*, 834*m*. ^{1}H-NMR (^{1}H,^{1}H-COSY, 400 MHz): 5.05 (*m*, H–C(5), H–C(9), H–C(13)); 2.57 (*t*, J = 7.4, 2 H–C(3)); 2.27–2.22 (*q*, 2 H–C(4)); 2.23 (*s*, Me–C(2)); 2.01–1.92 (*m*, 2 H–C(7), 2 H–C(8), 2 H–C(11), 2 H–C(12)); 1.63 (*s*, 3 H–C(15)); 1.59 (*s*, Me–C(6)); 1.56 (*s*, Me–C(10), Me–C(14)). ^{13}C-NMR (BB, DEPT, ^{13}C,^{1}H-COSY, 100.6 MHz): 181.65 (C(2)); 138.42 (C(6)); 135.00 (C(10)); 130.88 (C(14)); 124.11 (C(13)); 123.57 (C(9)); 120.30 (C(5)); 111.68 (CN); 111.52 (CN); 85.84 (C(1)); 39.46 (C(7) or C(11)); 39.34 (C(7) or C(11)); 37.74 (C(3)); 26.50 (C(8) or C(12)); 26.22 (C(8) or C(12)); 25.87 (C(4)); 25.43 (C(15)); 22.31 (*Me*–C(2)); 17.40 (*Me*–C(14)); 15.80 (*Me*–C(6) or *Me*–C(10)); 15.73 (*Me*–C(6) or *Me*–C(10)). MS: 310 (4, M^+, $C_{21}H_{30}N_2^+$), 199 (4), 137 (14), 136 (16), 123 (10), 81 (37), 69 (100), 55 (11), 41 (43).

General Procedure for the Irradiation of the Polyalkenes. Irradiations were performed in a *Rayonet-RPR-100* photochemical reactor equipped with sixteen 300- or 350-nm (λ_{max}) lamps of overall 1000 W output. To 150 ml of an Ar-flushed soln. of 3.0 mmol polyalkene in MeCN/H_2O 4:1 or MeCN/MeOH 4:1, 0.75 mmol of 2,3,5,6-tetramethylbenzene-1,4-dicarbonitrile and 0.85 mmol of biphenyl (0.1–0.2 mol-equiv.) were added. The transparent soln. was irradiated in a *Pyrex* or quartz immersion well with H_2O cooling, and the reaction was monitored by GLC and brought to > 95% conversion of polyalkene within 12–25 h. After repeated extractions with CH_2Cl_2, the org. phase was evaporated and the yellowish residue flash chromatographed (*Lobar* columns, *Merck* silica gel *60*, 0.040–0.063 mm, 150-fold, Et_2O/CH_2Cl_2 1:20) rendering the product fractions in > 96% purity as judged by GLC and ^{1}H-NMR.

c-*3-Hydroxy-2,2,*c-*6-trimethylcyclohexane-*r-*1-methyl Acetate* (**2**): See [1]. In addition, the structure of **2** was confirmed by X-ray analysis (see *Table*); crystallization from pentane/acetone gave colorless prisms. M.p. 57–58°.

2-(3-Hydroxy-1,2,2-trimethylcyclopentyl)propanedinitrile (**3**): The 1:1 mixture of 3α- and 3β-isomers[8]) was not separable by column chromatography.

3β-**3** (R = β-OH)[8]): ^{1}H-NMR (270 MHz): 4.39 (*s*, $CH(CN)_2$); 3.94 (*dd*, H–C(3)); 1.30 (*s*, Me–C(1)); 1.05 (*s*, 3 H); 0.99 (*s*, 3 H). ^{13}C-NMR (BB, DEPT, 67.9 MHz): 113.10 (CN); 113.00 (CN); 80.79 (C(3)); 48.02 (C); 47.39 (C); 34.78 (CH_2); 31.48 ($CH(CN)_2$); 29.32 (CH_2); 22.89 (Me); 20.24 (Me); 17.62 (Me).

3α-**3** (R = α-OH)[8]): ^{1}H-NMR (270 MHz): 3.86 (*dd*, H–C(3)); 3.62 (*s*, $CH(CN)_2$); 1.46 (*s*, Me–C(1)); 1.14 (*s*, 3 H); 0.98 (*s*, 3 H). ^{13}C-NMR (BB, DEPT, 67.9 MHz): 112.82 (CN); 112.34 (CN); 82.95 (CH, C(3)); 48.42 (C); 47.53 (C); 36.25 (CH_2); 31.78 ($CH(CN)_2$); 30.14 (CH_2); 24.23 (Me); 21.16 (Me); 18.32 (Me).

*2-(*c-*3-Methoxy-1,2,2-trimethyl-*r-*1-cyclopentyl)propanedinitrile* (**5**; R = β-MeO)[8]): M.p. 81°. IR: 2982*s*, 2968*s*, 2917*s*, 2250*m*, 1462*m*, 1382*s*, 1188*m*, 1168*m*, 1119*s*, 1111*s*, 1088*s*. ^{1}H-NMR (^{1}H,^{1}H-COSY, 270 MHz): 4.56 (*s*, $CH(CN)_2$); 3.35 (*m*, H–C(3)); 3.27 (*m*, MeO); 2.11–1.97 (*m*, H_α–C(4), 1 H–C(5)); 1.86–1.77 (*m*, 1 H–C(5)); 1.67–1.58 (*m*, H_β–C(4)); 1.30 (*s*, Me–C(1)); 1.05 (*s*, Me_α–C(2)); 0.97 (*s*, Me_β–C(2)). ^{13}C-NMR (BB, DEPT, ^{13}C,^{1}H-COSY, 67.9 MHz): 113.39 (CN); 113.22 (CN); 90.34 (C(3)); 57.66 (MeO); 48.34 (C(1) or C(2)); 48.00 (C(1) or C(2)); 35.13 (C(5)); 31.51 ($CH(CN)_2$); 26.07 (C(4)); 23.86 (Me_β–C(2)); 19.87 (*Me*–C(1)); 18.09 (Me_α–C(2)). MS: 206 (7, M^+, $C_{12}H_{18}N_2O^+$), 141 (7), 109 (18), 83 (69), 71 (100), 55 (17).

*2-(*t-*3-Methoxy-1,2,2-trimethyl-*r-*1-cyclopentyl)propanedinitrile* (**5**; R = α-MeO)[8]): M.p. 60–61°. IR: 2996*s*, 2970*s*, 2925*s*, 2260*w*, 2253*w*, 1463*m*, 1383*m*, 1371*m*, 1106*m*, 1086*s*. ^{1}H-NMR (^{1}H,^{1}H-COSY, 400 MHz): 3.60 (*s*,

$CH(CN)_2$); 3.29 (*dd*, $J = 6.8$, 3.3, H–C(3)); 3.25 (*s*, MeO); 2.07–1.98 (*m*, H_β–C(4)); 1.92–1.85 (*m*, H_α–C(5)); 1.82–1.77 (*m*, H_β–C(5)); 1.74–1.66 (*m*, H_α–C(4)); 1.40 (*s*, Me–C(1)); 1.11 (*s*, Me_α–C(2)); 0.99 (*s*, Me_β–C(2)); NOE (400 MHz, saturation → enhancement): 3.60 ($CH(CN)_2$) → 3.29 (*w*, H–C(3)), 1.82–1.77 (*m*, H_β–C(5)), and 0.99 (*s*, Me_β–C(2)); 3.29 (H–C(3)) → 2.07–1.98 (*s*, H_β–C(4)), 1.74–1.66 (*s*, H_α–C(4)), and 0.99 (*s*, Me_β–C(2)); 1.40 (Me–C(1)) → 3.60 (*m*, $CH(CN)_2$), 3.25 (*m*, MeO), 1.92–1.85 (*m*, H_α–C(5)), and 1.11 (*s*, Me_α–C(2)); 1.11 (Me_α–C(2)) → 3.25 (*s*, MeO), 1.40 (*s*, Me–C(1)), and 0.99 (*m*, Me_β–C(2)); 0.99 (Me_β–C(2)) → 3.60 (*s*, $CH(CN)_2$) and 3.29 (*s*, H–C(3)). ^{13}C-NMR (**BB**, DEPT, ^{13}C,^{1}H-COSY, 100.6 MHz): 112.93 (CN); 112.39 (CN); 91.86 (C(3)); 57.58 (MeO); 48.45 (C(1) or C(2)); 47.75 (C(1) or C(2)); 36.21 (C(5)); 31.59 ($CH(CN)_2$); 26.71 (C(4)); 24.77 (Me_β–C(2)); 20.95 (Me–C(1)); 18.50 (Me_α–C(2)). MS: 206 (6, M^+, $C_{12}H_{18}N_2O^+$), 109 (18), 83 (67), 71 (100), 41 (16).

2,6-Dimethylhepta-1,5-diene-3,3-dicarbonitrile (**6**): IR: 2972*s*, 2926*s*, 2249*w*, 1727*m*, 1673*m*, 1651*m*, 1452*m*, 1385*s*, 922*s*, 838*m*. ^{1}H-NMR (^{1}H,^{1}H-COSY, 400 MHz): 5.47 (*s*, H–C(1) *cis* to C(3)); 5.26 (*s*, H–C(1) *trans* to C(3)); 5.18 (*t*, H–C(5)); 2.75 (*d*, $J = 7.5$, 2 H–C(4)); 1.95 (*s*, Me–C(2)); 1.78 (*s*, 3 H–C(7)); 1.70 (*s*, Me–C(6)). ^{13}C-NMR (**BB**, DEPT, ^{13}C,^{1}H-COSY, 100.6 MHz): 140.58 (C(2)); 134.82 (C(6)); 117.88 (C(1)); 114.36 (C(4)); 114.32 (2 CN); 43.58 (C(3)); 36.05 (C(4)); 25.87 (C(7)); 18.35 (Me–C(2)); 18.24 (Me–C(6)). MS: 174 (1, M^+, $C_{11}H_{14}N_2^+$), 69 (100), 41 (62), 39 (16).

*2-(2,3,*t*-3a,4,5,6,7,7a-Octahydro-*c*-5-hydroxy-1,4,4,*c*-7a-tetramethyl-1*H*-inden-*r*-1-yl)propanedinitrile* (**9**; see also *Fig.* and *Table*): M.p. 157–161°. IR: 3529*s*, 2985*s*, 2962*s*, 2945*s*, 2262*w*, 1455*s*, 1385*s*, 1072*m*, 1030*s*. ^{1}H-NMR (^{1}H,^{1}H-COSY, 400 MHz): 3.75 (*s*, $CH(CN)_2$); 3.24 (*dd*, $J = 11.2$, 5.5, H–C(5)); 1.80–1.41 (*m*, 9 H); 1.36 (*s*, 3 H); 0.98 (*s*, 3 H); 0.96 (*s*, 3 H); 0.89 (*s*, 3 H). ^{13}C-NMR (**BB**, DEPT, ^{13}C,^{1}H-COSY, 100.6 MHz): 113.62 (CN); 113.10 (CN); 79.11 (C(5)); 53.31 (C(3a)); 50.67 (C); 45.57 (C); 38.45 (C); 35.73 (CH_2); 32.52 ($CH(CN)_2$); 32.24 (CH_2); 29.49 (Me); 28.29 (CH_2); 21.13 (Me); 20.62 (CH_2); 16.64 (Me); 15.77 (Me). MS: 260 (2, M^+, $C_{16}H_{24}N_2O^+$), 242 (7), 227 (8), 154 (67), 136 (59), 121 (50), 95 (100), 82 (16), 67 (15), 57 (33), 41 (40).

*2-(2,3,*c*-3a,4,5,6,7,7a-Octahydro-*t*-5-hydroxy-1,4,4,*c*-7a-tetramethyl-1*H*-inden-*r*-1-yl)propanedinitrile* (**10**): M.p. 91–93°. IR: 3535*s*, 2988*m*, 2957*s*, 2259*w*, 1471*m*, 1384*m*, 1061*m*, 1004*m*, 927*m*. ^{1}H-NMR (^{1}H,^{1}H-COSY, 400 MHz): 3.66 (*s*, $CH(CN)_2$); 3.48 (*m*, H–C(5)); 2.29–2.22 (*m*, 1 H); 1.99–1.60 (*m*, 7 H); 1.80–1.76 (*m*, H–C(3a)); 1.21 (*s*, Me–C(1)); 1.15 (*s*, Me–C(7a)); 1.07–1.02 (*m*, 1 H); 1.02 (*s*, Me_α–C(4)); 0.96 (*s*, Me_β–C(4)); NOE (400 MHz, saturation → enhancement): 3.66 ($CH(CN)_2$) → 1.80–1.76 (*s*, H–C(3a)), 1.21 (*m*, Me–C(1)), and 1.15 (*s*, Me–C(7a)); 3.48 (H–C(5)) → 1.02 (*m*, Me_α–C(4)) and 0.96 (*s*, Me_β–C(4)); 1.21 (Me–C(1)) → 3.66 (*s*, $CH(CN)_2$); 1.15 (Me–C(7a)) → 3.66 (*s*, $CH(CN)_2$), 1.80–1.76 (*m*, H–C(3a)), and 0.96 (*s*, Me_β–C(4)); 1.02 (Me_α–C(4)) → 3.48 (*m*, H–C(5)), and 1.80–1.76 (*w*, H–C(3a)); 0.96 (Me_β–C(4)) → 3.48 (*s*, H–C(5)), 1.80–1.76 (*s*, H–C(3a)), and 1.15 (*s*, Me–C(7a)). ^{13}C-NMR (**BB**, DEPT, ^{13}C,^{1}H-COSY, 100.6 MHz): 113.68 (CN); 113.46 (CN); 74.18 (C(5)); 53.73 (C); 52.26 (C(3a)); 45.83 (C); 36.26 (C); 33.68 (CH_2); 31.21 ($CH(CN)_2$); 29.22 (Me_β–C(4)); 25.96 (Me_α–C(4)); 25.89 (CH_2); 24.45 (CH_2); 24.09 (CH_2); 21.70 (Me–C(7a)); 18.66 (Me–C(1)). MS: 260 (2, M^+, $C_{16}H_{24}N_2O^+$), 242 (15), 227 (11), 177 (55), 173 (10), 154 (49), 139 (21), 121 (72), 95 (60), 81 (62), 67 (52), 55 (63), 41 (100).

*Ethyl 1,2,3,4,*t*-4a,4b,5,6,7,8,*t*-8a,9,10,10a-Tetradecahydro-*c*-7-hydroxy-*c*-2,*c*-4b,8,8,*c*-10a-pentamethylphenanthrene-*r*-1-carboxylate* (1β-**12b** and 1α-**12b**)[7][8]: The 3:1 mixture of 1β- and 1α-**12b** was not separable by column chromatography or by HPLC. IR: 3500–3422*w* (br.), 2924*s*, 2852*s*, 1722*s*, 1648*w*, 1449*s*, 1384*m*, 1147*m*, 1035*m*, 908*m*, 734*s*. ^{1}H-NMR (^{1}H,^{1}H-COSY, 400 MHz): 1α-**12b**: 4.07 (*q*, $J = 6$, MeCH_2O); 3.17 (*dd*, $J = 6$, 10, 1 H); 2.20–0.70 (br. *m*, 17 H); 1.21 (*t*, $J = 6$, MeCH$_2$O); 0.92 (*s*, 3 H); 0.86 (*s*, 3 H); 0.82 (*s*, 3 H); 0.76 (*s*, 3 H); 0.75 (*s*, 3 H); 1β-**12b**: 4.07 (*q*, $J = 6$, MeCH_2O); 3.17 (*dd*, $J = 6$, 10, 1 H); 2.20–0.70 (br. *m*, 17 H); 1.21 (*t*, $J = 6$, MeCH$_2$O); 0.97 (*s*, 3 H); 0.96 (*s*, 3 H); 0.92 (*d*, $J = 7$, 3 H); 0.81 (*s*, 3 H); 0.74 (*s*, 3 H). ^{13}C-NMR (**BB**, DEPT, 100.6 MHz): 1α-**12b**: 173.72 (C,CO); 78.89 (CH); 60.38 (CH); 59.64 (CH); 59.40 (CH_2); 55.65 (CH); 41.21 (CH_2); 41.12 (CH_2); 38.86 (C); 38.28 (CH_2); 37.80 (C); 36.73 (C); 33.93 (CH_2); 31.66 (CH); 27.94 (Me); 21.90 (Me); 17.50 (CH_2); 17.21 (Me); 17.10 (Me); 16.33 (CH_2); 15.35 (Me); 14.31 (Me); 1β-**12b**: 174.13 (C, CO); 78.85 (CH); 65.14 (CH); 59.51 (CH_2); 58.85 (CH); 55.50 (CH); 41.37 (CH_2); 38.78 (C); 38.36 (CH_2); 37.37 (C); 37.25 (C); 36.59 (CH_2); 29.73 (CH); 28.06 (Me); 27.16 (CH_2); 20.59 (Me); 19.74 (CH_2); 18.11 (CH_2); 16.29 (Me); 15.31 (2 Me); 14.43 (Me). MS (both isomers): 350 (20, M^+, $C_{22}H_{38}O_3^+$), 332 (31), 207 (100), 189 (62), 135 (50), 121 (52), 109 (46), 95 (51), 81 (50), 55 (56), 41 (41), 29 (26).

*Ethyl 2,3,3a,4,5,*c*-5a,6,7,8,9,9a,*c*-9b-Dodecahydro-*t*-7-hydroxy-3,*t*-3a,6,6,*t*-9a-pentamethyl-1*H*-cyclopenta[a]naphthalene-*r*-3-acetate* (**13b**)[8]: IR: 3452*m* (br.), 2964*s*, 2940*s*, 2873*s*, 1730*s*, 1647*w*, 1465*m*, 1450*m*, 1385*m*, 1368*m*, 1147*m*, 1107*m*, 1034*m*, 918*w*, 734*m*. ^{1}H-NMR (^{1}H,^{1}H-COSY, 400 MHz): 4.09 (*q*, $J = 7$, MeCH_2O); 3.17 (*dd*, $J = 7$, 10, H–C(7)); 2.44–0.74 (br. *m*, 14 H); 2.31 (*d*, $J = 12$, 1 H, CH_2COOEt); 2.14 (*d*, $J = 12$, 1 H, CH_2COOEt); 1.23 (*t*, $J = 7$, MeCH$_2$O); 0.99 (*s*, Me–C(3)); 0.95 (*s*, Me_α–C(6)); 0.87 (*s*, Me–C(9a)); 0.83 (*s*, Me–C(3a)); 0.77 (*s*, Me_β–C(6)); 0.69 (*dd*, $J = 4$, 12, H–C(5a)); NOE (400 MHz, saturation → enhancement): 3.17

(H–C(7)) → 0.69 (*m*, H–C(5a)), 0.95 (*s*, Me_α–C(6)), and 1.06 (*w*, H_α–C(9)); 0.99 (Me–C(3)) → 0.83 (*s*, Me–C(3a)), and 2.14 (*m*, CH_2COOEt); 0.95 (Me_α–C(6)) → 0.77 (*s*, Me_β–C(6)), 0.69 (*w*, H–C(5a)), and 3.17 (*m*, H–C(7)); 0.87 (Me–C(9a)) → 0.77 (*s*, Me_β–C(6)); 0.83 (Me–C(3a)) → 0.99 (*s*, Me–C(3)); 0.77 (Me_β–C(6)) → 0.95 (*s*, Me_α–C(6)), and 0.87 (*s*, Me–C(9a)). ^{13}C-NMR (BB, DEPT, ^{13}C,^{1}H-COSY, 100.6 MHz): 173.72 (CO); 79.15 (C(7)); 59.92 (MeCH_2O); 57.32 (C(9b)); 56.30 (C(5a)); 46.36 (C); 45.55 (C); 42.88 (CH_2COOEt); 39.09 (CH_2); 38.76 (C); 36.75 (C); 33.37 (CH_2); 33.12 (CH_2); 28.08 (Me_α–C(6)); 27.14 (CH_2); 22.0 (*Me*–C(3)); 20.24 (CH_2); 18.92 (CH_2); 17.59 (*Me*–C(3a)); 16.22 (*Me*–C(9a)); 15.26 (Me_β–C(6)); 14.29 (*Me*CH_2O). MS: 350 (14, M^+, $C_{22}H_{38}O_3^+$), 332 (53), 207 (100), 189 (85), 161 (34), 135 (68), 121 (70), 95 (71), 81 (67), 43 (83).

*2-(2,3,3a,4,5,*t*-5a,6,7,8,9,9a,*t*-9b-Dodecahydro-*c*-7-hydroxy-3,*c*-3a,6,6,*c*-9a-pentamethylcyclopenta[*a*]naphthalen-*r*-3-yl)propanedinitrile* (**13c**)[8]: M.p. 239–241°. IR: 3445 (br.), 2993*m*, 2941*s*, 2255*w*, 1455*m*, 1385*s*, 1046*s*, 1025*m*. ^{1}H-NMR (^{1}H,^{1}H-COSY, 400 MHz): 3.74 (*s*, CH(CN)$_2$); 3.20 (*dd*, *J* = 5.5, 11, H–C(7)); 1.82–1.79 (*dd*, *J* = 3, 9.5, 1 H); 1.74–1.70 (*m*, 2 H); 1.67–1.60 (*m*, 4 H); 1.58–1.52 (*m*, 2 H, therein H–C(9b)); 1.51–1.49 (*dd*, *J* = 3, 7, 1 H); 1.46–1.41 (*m*, 2 H); 1.36 (*s*, Me–C(3)); 1.07–1.00 (*m*, 1 H); 0.97 (*s*, Me_α–C(6)); 0.96 (*s*, Me–C(3a)); 0.89 (*s*, Me–C(9a)); 0.78 (*s*, Me_β–C(6)); 0.76 (*m*, H–C(5a)); NOE (400 MHz, saturation → enhancement): 3.74 (CH(CN)$_2$) → 1.36 (*m*, Me–C(3)) and 0.96 (*s*, Me–C(3a)); 3.20 (H–C(7)) → 0.97 (*s*, Me_α–C(6)), 0.78 (*m*, Me_β–C(6)), and 0.76 (*w*, H–C(5a)); 1.36 (Me–C(3)) → 1.58–1.52 (*m*, H–C(9b)); 0.97 (Me_α–C(6)) → 3.20 (*m*, H–C(7)), 0.78 (*m*, Me_β–C(6)), and 0.76 (*m*, H–C(5a)); 0.96 (Me–C(3a)) → 3.74 (*s*, CH(CN)$_2$) and 0.89 (*s*, Me–C(9a)); 0.89 (Me–C(9a)) → 0.96 (*s*, Me–C(3a)) and 0.78 (*s*, Me_β–C(6)); 0.78 (Me_β–C(6)) → 0.97 (*s*, Me_α–C(6)) and 0.89 (*s*, Me–C(9a)); 0.76 (H–C(5a)) → 3.20 (*m*, H–C(7)), 1.58–1.52 (*m*, H–C(9b)), and 0.97 (*m*, Me_α–C(6)). ^{13}C-NMR (BB, DEPT, ^{13}C,^{1}H-COSY, 100.6 MHz): 113.02 (CN); 112.42 (CN); 78.88 (C(7)); 57.48 (C(9b)); 55.90 (C(5a)); 49.18 (C); 46.10 (C); 38.97 (CH_2); 38.71 (CH_2); 36.91 (C); 35.82 (CH_2); 34.17 (CH_2); 31.55 (*C*H(CN)$_2$); 28.00 (Me_α–C(6)); 26.97 (CH_2); 21.77 (*Me*–C(3)); 19.27 (CH_2); 18.77 (CH_2); 17.38 (*Me*–C(3a)); 16.19 (*Me*–C(9a)); 15.24 (Me_β–C(6)). MS: 328 (1, M^+, $C_{21}H_{32}N_2O$), 310 (2), 295 (18), 207 (100), 189 (50), 161 (16), 139 (54), 107 (44), 95 (32), 81 (23), 69 (31), 55 (32), 43 (39).

Acetylation of **3**. Freshly distilled acetyl chloride (1 ml, 14.06 mmol) was dropwise added under Ar to a stirred 1:1 mixture **3** in CH_2Cl_2 (20 ml) and pyridine (1 ml), at 0° during 15 min. The mixture was stirred for 1.5 h and then poured into cold H_2O before extraction with CH_2Cl_2 (3 ×). The combined org. layer was washed with sat. $NaHCO_3$ soln. (3 ×) and H_2O (1 ×), dried (Na_2SO_4), and evaporated and the oily residue flash chromatographed (*Lobar* columns, 80 g of silica gel *60* (*Merck*, 0.040–0.063 mm), Et_2O/CH_2Cl_2 1:20 → 1:10): 321 mg of pure 3β-**4** (R = β-AcO[8]); light yellowish oil, 45%) and 349 mg of 3α-**4** (R = α-AcO[8]); solid, 49%).

*2-(*c*-3-Acetoxy-1,2,2-trimethyl-*r*-1-cyclopentyl)propanedinitrile* (3β-**4**): IR: 2975*s*, 2930*m*, 2253*w*, 1734*s*, 1473*m*, 1456*m*, 1401*s*, 1247*s*, 1037*s*. ^{1}H-NMR (^{1}H,^{1}H-COSY, 400 MHz): 4.93 (*dd*, H–C(3)); 3.94 (*s*, CH(CN)$_2$); 2.32–2.21 (*m*, H_α–C(4)); 2.06 (*s*, MeCOO); 1.97–1.92 (*m*, H_β–C(5)); 1.84–1.76 (*m*, H_α–C(5)); 1.57–1.49 (*m*, H_β–C(4)); 1.34 (*s*, Me–C(1)); 1.06 (*s*, Me_α–C(2)); 1.02 (*s*, Me_β–C(2)); NOE (400 MHz, saturation → enhancement): 4.93 (H–C(3)) → 2.32–2.21 (*s*, H_α–C(4)); 3.94 (MeCOO) → 1.97–1.92 (*w*, H_β–C(5)) and 1.02 (*s*, Me_β–C(2)); 1.80 (H_α–C(5)) → 2.32–2.21 (*w*, H_α–C(4)); 1.34 (Me–C(1)) → 4.93 (*s*, H–C(3)), 1.84–1.76 (*s*, H_α–C(5)), and 1.06 (*s*, Me_α–C(2)); 1.06 (Me_α–C(2)) → 4.93 (*s*, H–C(3)) and 1.34 (*s*, Me–C(1)); 1.02 (Me_β–C(2)) → 3.94 (*s*, CH(CN)$_2$). ^{13}C-NMR (BB, DEPT, ^{13}C,^{1}H-COSY, 100.6 MHz): 170.17 (Me*C*OO); 112.49 (CN); 112.31 (CN); 81.25 (C(3)); 47.74 (C(1) or C(2)); 46.51 (C(1) or C(2)); 34.68 (C(5)); 31.20 (*C*H(CN)$_2$); 26.47 (C(4)); 22.37 (Me_α–C(2)); 21.02 (*Me*COO); 20.30 (*Me*–C(1)); 18.15 (Me_β–C(2)). MS: 234 (1, M^+, $C_{13}H_{18}N_2O_2^+$), 164 (1), 127 (12), 109 (11), 83 (11), 43 (100).

*2-(*t*-3-Acetoxy-1,2,2-trimethyl-*r*-1-cyclopentyl)propanedinitrile* (3α-**4**): IR: 2975*m*, 2262*w*, 1733*s*, 1378*m*, 1245*s*, 1216*m*, 1028*m*. ^{1}H-NMR (^{1}H,^{1}H-COSY, 400 MHz): 4.91 (*dd*, H–C(3)); 3.66 (*s*, CH(CN)$_2$); 2.32–2.19 (*m*, H_β–C(4)); 2.05 (*s*, MeCOO); 1.99–1.88 (*m*, H_α–C(5)); 1.86–1.75 (*m*, H_β–C(5)); 1.73–1.64 (*m*, H_α–C(4)); 1.44 (*s*, Me–C(1)); 1.09 (*s*, Me_α–C(2)); 1.05 (*s*, Me_β–C(2)); NOE (400 MHz, saturation → enhancement): 4.91 (H–C(3)) → 3.66 (*s*, CH(CN)$_2$), 2.32–2.19 (*s*, H_β–C(4)), and 1.05 (*s*, Me_β–C(2)); 3.66 (CH(CN)$_2$) → 4.91 (*m*, H–C(3)), 1.86–1.75 (*m*, H_β–C(5)), and 1.05 (*s*, Me_β–C(2)); 1.44 (Me–C(1)) → 1.99–1.88 (*m*, H_α–C(5)) and 1.09 (*s*, Me_α–C(2)); 1.09 (*s*, Me_α–C(2)) → 4.91 (*m*, H–C(3)), 3.66 (*m*, CH(CN)$_2$), and 1.44 (*m*, Me–C(1)). ^{13}C-NMR (BB, DEPT, ^{13}C,^{1}H-COSY, 100.6 MHz): 170.16 (Me*C*OO); 112.56 (CN); 112.00 (CN); 83.68 (C(3)); 48.42 (C(1) or C(2)); 47.18 (C(1) or C(2)); 36.28 (C(5)); 31.35 (*C*H(CN)$_2$); 28.08 (C(4)); 24.30 (Me_β–C(2)); 21.10 (*Me*COO); 20.51 (*Me*–C(1)); 18.36 (Me_α–C(2)). MS: 234 (1, M^+, $C_{13}H_{18}N_2O_2^+$), 192 (2), 127 (16), 109 (14), 83 (14), 43 (100).

REFERENCES

[1] U. Hoffmann, Y. Gao, B. Pandey, S. Klinge, K.-D. Warzecha, C. Krüger, H. D. Roth, M. Demuth, *J. Am. Chem. Soc.* **1993,** *115,* 10358.

[2] For a survey on PET processes, see 'Photoinduced Electron Transfer', Eds. M. A. Fox and M. Chandon, Elsevier, Amsterdam, 1988, Part C.

[3] For a survey on radical cations, see H. D. Roth, *Topics Curr. Chem.* **1992,** *163,* 131–245.

[4] For *anti-Markovnikov* interception of radical cations by nucleophiles, see R. A. Neunteufel, D. R. Arnold, *J. Am. Chem. Soc.* **1973,** *95,* 4080; A. J. Maroulis, J. Shigemitsu, D. R. Arnold, *ibid.* **1978,** *100,* 535; P. G. Gassman, K. D. Olson, L. Walter, R. Yamaguchi, *ibid.* **1981,** *103,* 4977.

[5] X. Xing, Ph.D. Thesis, Max-Planck-Institut für Strahlenchemie/University of Essen, in progress.

[6] P. G. Gassman, S. A. De Silva, *J. Am. Chem. Soc.* **1991,** *113,* 9870.

[7] K.-D. Warzecha, Ph.D. Thesis, Max-Planck-Institut für Strahlenchemie/University of Essen, in progress.

[8] R. C. Cookson, V. N. Gogte, J. Hudec, N. A. Mirza, *Tetrahedron Lett.* **1965,** 3955.

[9] D. D. M. Wayner, D. J. McPhee, D. Griller, *J. Am. Chem. Soc.* **1988,** *110,* 132.

[10] C. Rüchardt, H.-D. Beckhaus, *Topics Curr. Chem.* **1986,** *130,* 1.

[11] 'Enantiomers, Racemates, and Resolutions', Eds. J. Jacques, A. Collet, and S. H. Wilen, Kriefer Press, Florida, 1994, p. 53.

[12] G. Ourisson, M. Rohmer, K. Poralla, *Ann. Rev. Microbiol.* **1987,** 301; I. Abe, M. Rohmer, G. D. Prestwich, *Chem. Rev.* **1993,** *93,* 2189.

[13] a) A. Eschenmoser, L. Ruzicka, O. Jeger, D. Arigoni, *Helv. Chim. Acta* **1955,** *38,* 1890; b) G. Stork, A. W. Burgstahler, *J. Am. Chem. Soc.* **1955,** *77,* 5068.

[14] H. Suzuki, K. Nakamura, R. Gota, *Bull. Chem. Soc. Jpn.* **1966,** *39,* 128.

[15] H. Suzuki, T. Hanafusa, *Synthesis* **1974,** *1,* 53.

[16] L. Friedman, H. Shechter, *J. Org. Chem.* **1961,** *26,* 2522.

[17] a) E. E. van Tamelen, R. G. Nadeau, *Bioorg. Chem.* **1982,** *11,* 197; b) E. E. van Tamelen, S. A. Marson, *ibid.* **1982,** *11,* 219.

[18] S. Klinge, M. Demuth, *Synlett* **1993,** 783.