The angle between the S—P—N(1) and C—P—N(2) planes is 92.9°. In contrast to the planar ring containing the Si atom, the other ring is puckered (angle between the planes S—Mn—N(1) and S—P—N(1) = 20.8°).

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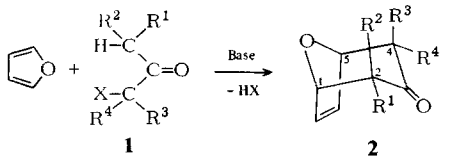
[6] ^{1}H-NMR [$C_6D_5CD_3$; −60°C: δ = 0.45 (s, 18H), 0.22 (s, 9H), −0.17 (s, 9H); 20°C: δ = 0.45 (s, 18H), 0.24 (s, 18H)]. ^{31}P{^{1}H}-NMR [$C_6D_5CD_3$; −60°C as well as 20°C: δ = −1.6 (s)]. ^{13}C{^{1}H}-NMR [$C_6D_5CD_3$; −60°C: δCO = 227 (s); the appearance of a single CO signal is an indication of a *trans*-configuration in **3**]. IR [*n*-hexane; metalcarbonyl region: ν = 2030 (s), 1935 (vs), 1904 (w) cm^{-1}].

Efficient Synthesis of 8-Oxabicyclo[3.2.1]oct-6-en-3-ones, Preparatively Useful [4+3]-Cycloadducts**

By *Baldur Föhlisch**, *Eberhard Gehrlach*, and *Rolf Herter*

The title compounds **2**, accessible by cycloaddition of allylium-2-olates to furans have proven to be valuable educts for the synthesis of natural products and biologically active analogues. Previously, however, the cycloadducts could only be synthesized using tedious and expensive methods[2a,3a,4,5,7]. We have now found a method in which not only α-bromoketones but also the less expensive and more stable α-chloroketones can be reacted with readily available bases.

The α-haloketones **1a–h** react with furan in 2,2,2-trifluoroethanol (TFE), a very weakly nucleophilic and powerful ionizing solvent, in the presence of triethylamine or sodium 2,2,2-trifluoroethoxide generated *in situ* to give 8-oxabicyclo[3.2.1]oct-6-en-3-ones **2** (Table 1). The yields are good, and work-up is simple. The bicyclic compounds **2b—f** are formed stereoselectively. By reduction of **2f** or **2g** with the Zn/Cu couple, the unsubstituted ketone **2**, $R^1 - R^4 = H$, is also accessible in good yields. α-Chloroketones can not only be prepared by chlorination of ketones, but also *via* several other routes, by C—C coupling reactions. Thus, the [4+3]-cycloaddition of allylium-2-olates opens up promising applications in synthetic chemistry.



1 **2**

	R^1	R^2	R^3	R^4	X		R^1	R^2	R^3	R^4	X
a	CH_3	CH_3	H	H	Cl	**e**	CH_3	CH_3	H	CH_3	Cl
b	CH_3	H	H	CH_3	Cl	**f**	Cl	Cl	H	Cl	Cl
c	CH_3	H	H	CH_3	Br	**g**	Cl	Cl	Cl	Cl	Cl
d	CH_3	H	CH_3	CH_3	Cl	**h**	H	—$(CH_2)_3$—		H	Br

Table 1. 8-Oxabicyclo[3.2.1]oct-6-en-3-ones **2** by reaction of α-haloketones **1** and furan in TFE/furan (1:1 v/v) at room temperature with triethylamine (Method A: molar ratio 1:2) or sodium trifluoroethoxide (Method B: molar ratio 1:1) as base. All products except **2g** are known.

Educt **1**	Method	Reaction time	Product **2**	Yield [%]	*T* [°C/torr] [a] M.p. [°C]
a	A	25 d	**a**	45	120–140/12
a	B	29 d	**a**	56	41–42
b	A	5 d	**b** [b]	77	120–140/12
b	B	6 d	**b** [b]	80	33–35
c	B	1 d	**c** ≡ **b** [b]	93	
d	A	4 d	**d**	73	130–150/12
d	B	3 d	**d**	91	70–90/0.3
e	A	10 d	**e** ≡ **d**	68	13–16
f	A	75 min	**f**	55	70–90/0.001 88–89
g	A	75 min	**g** [c]	52	90–120/0.001 88–89
h	A	1 d	**h**	84	60–70/0.002 43–44

[a] Kugelrohr temperature. [b] The product contains at maximum 6% of the C-2/C-4 epimers. M.p. of isomerically pure **2b**: 45–46°C. [c] ^{1}H-NMR ($CDCl_3$): δ = 5.25 (s, 1-H, 5-H), 6.65 (s, 6-H, 7-H); IR ($CHCl_3$): 1765 cm^{-1} (C=O).

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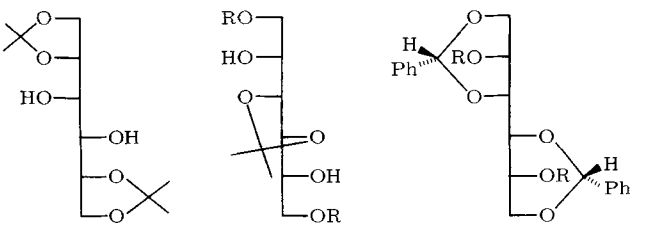
Optically Active Glycerol Derivatives from 1,3(*R*):4,6(*R*)-Di-*O*-benzylidene-D-mannitol—The First Structural Analogues of Moenomycin A**

By *Thomas Schubert* and *Peter Welzel**

Morpain and *Tisserand* recently reported[5] that optically active glycerides are accessible from D-mannitol derivatives of type **2** in fewer steps than from the "classical" educt **1**[1]. Presumably, di-*O*-benzylidene compound **3** is



1 **2** **3**, R = H; **4**, R = $C_{18}H_{37}$; **5**, R = $C_{20}H_{41}$

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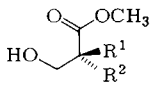
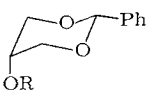
an even better starting material. Certain types of optically active glycerol derivatives can be prepared from **3** with a minimum of protecting group chemistry. Starting from **3** we have synthesized **6** and **7**, as well as **15**, a structural analogue of the antibiotic moenomycin A[6].

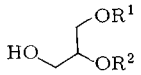
Alkylation of **3**[8] with 1-bromooctadecane or with 2,3-dihydrophytyl bromide in dimethylformamide afforded **4** (81%) and **5** (70%), respectively. Hydrolytic cleavage of the benzylidene protecting groups, followed by diol cleavage with sodium metaperiodate, subsequent oxidation of the aldehyde with silver(II) oxide and esterification of the resulting acid then furnished the *R*-glyceric acid derivatives **6** (36%) and **7** (56%), respectively.



6, R^1 = H, R^2 = $OC_{18}H_{37}$
7, R^1 = H, R^2 = $OC_{20}H_{41}$
8, R^1, R^2 = H, $OC_{18}H_{37}$



9, R = H
10, R = $C_{18}H_{37}$

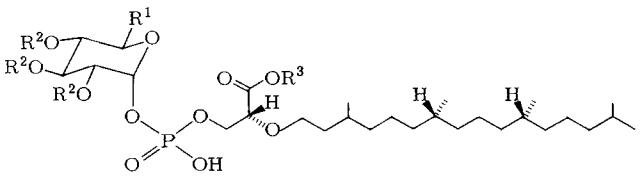


11, R^1 = COC_6H_5, R^2 = $C_{18}H_{37}$
12, R^1 = $COCH_3$, R^2 = $C_{18}H_{37}$

The racemic ester **8** was synthesized from *cis*-5-hydroxy-2-phenyl-1,3-dioxane **9**. *O*-Alkylation with 1-chlorooctadecane (phase-transfer catalysis) furnished **10** in 67% yield. Deslongchamps opening[14] of **10** to the hydroxybenzoate **11**, Jones oxidation, and esterification of the acid afforded the racemic ester **8** (51%, referred to **10**). **8** is also accessible in a total yield of 61% from **10** by hydrolytic cleavage of the benzylidene group, monoacetylation to **12**, Jones oxidation, and subsequent esterification.

In presence of the optically active shift reagent Eu(tfc)$_3$ the ^{1}H-NMR spectrum of **8** shows two OCH_3 signals (ratio: 1 : 1), while the spectrum of **6** recorded under the same conditions shows only one: hence, within the limits of NMR detection, **6** is formed in optically pure form.

For the preparation of **15**, **7** was allowed to react with 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl 1-phosphate according to the phosphoric acid diester method using 2,4,6-triisopropylbenzenesulfonyl chloride to give the diester **13**. Cleavage of the protecting groups with lithium hydroxide yielded the dilithium salt of **14**, which was converted by catalytic oxidation into the glucuronic acid derivative **15** (after ion-exchange).



13, R^1 = CH_2OAc, R^2 = Ac, R^3 = CH_3
14, R^1 = CH_2OH, R^2 = H, R^3 = H
15, R^1 = COOH, R^2 = H, R^3 = H

The antibiotic moenomycin A is one of the most active inhibitors of bacterial cell-wall biosynthesis[6]. However, a correlation between its very complex structure and biological activity has thus far been lacking. The synthetic access to model substances such as **15** now opens up the possibility of investigating this problem experimentally.

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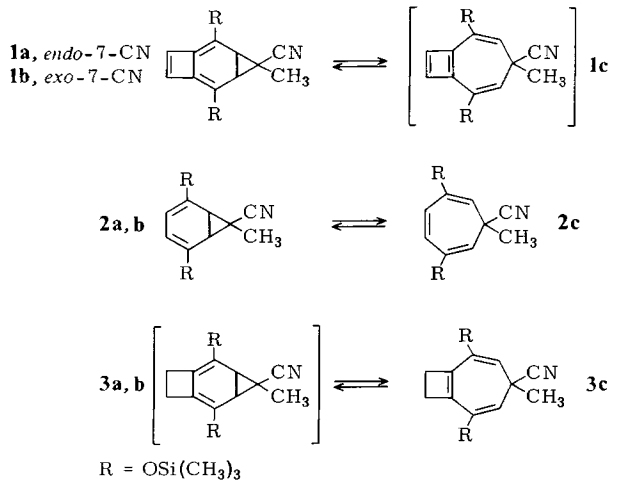
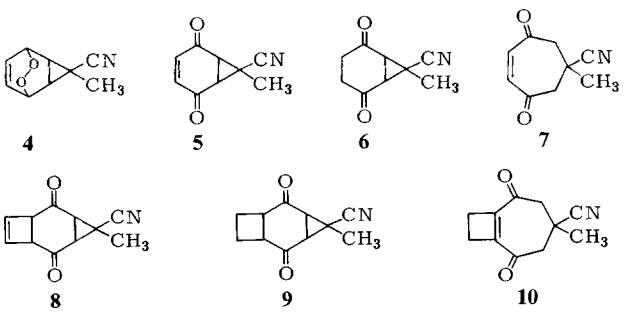
The Effect of an Annelated Cyclobutene or Cyclobutadiene Ring on the Norcaradiene—Cycloheptatriene Equilibrium**

By *Frank-Gerrit Klärner**, *Eckhart K. G. Schmidt*, and *Mahmoud Abdel Rahman*

The question of the antiaromaticity of 1,3-cyclobutadiene has been the subject of repeated theoretical and experimental investigations[1]. In the valence tautomeric equilibrium **1a, b** ⇌ **1c**, the cycloheptatriene derivative **1c** contains a cyclobutadiene ring as a subunit. Provided that cyclobutadiene is antiaromatic, the equilibrium is expected to be shifted in favor of the norcaradienes **1a** and **1b**. We report here on the syntheses and properties of the systems **1, 2,** and **3.**



The syntheses of **1, 2,** and **3** start from 7-methyl-1,3,5-cycloheptatrien-7-carbonitrile[3]. Addition of $^1O_2$ leads to **4** (yield 96%), which on subsequent reduction ($(NH_2)_2CS$ or Pt/H_2) and oxidation (MnO_2 or CrO_3) is converted into **5** (64%) or **6** (54%), respectively. Photochemical addition of



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