Stereoselective Connection of a C_2- and a Linear C_n-Unit to a Cyclopropane by a Formal Twofold Nucleophilic Substitution

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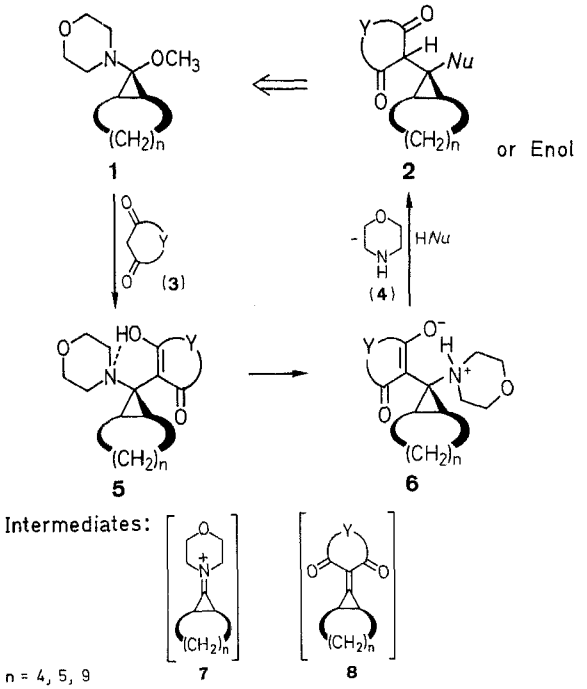
Bicyclo[4.1.0]heptan-7-one *O,N*-acetals such as 7-methoxy-7-morpholinobicyclo[4.1.0]heptane can be easily converted into 7-substituted 7-(2-oxoalkyl)bicyclo[4.1.0]heptanes via a formal twofold nucleophilic substitution. In the first reaction step, the methoxy group of the *O,N*-acetal is replaced by the 2,2-dimethyl-4,6-dioxo-1,3-dioxan-5-yl group by reaction with Meldrum's acid; in the second step, the morpholino group is replaced by a 2-oxoalkyl group by reaction with a 2-alkanone or an enamine. The resultant 2,2-dimethyl-4,6-dioxo-5-[7-(2-oxoalkyl)bicyclo[4.1.0]hept-7-yl]-1,3-dioxanes can be selectively reduced to the corresponding 2-hydroxyalkyl derivatives which readily undergo lactone formation with degradation of the Meldrum's acid moiety, or they can be thermally degradated in the presence of morpholine to give 7-(2-oxoalkyl)bicyclo[4.1.0]heptane-7-acetic acid morpholides. Thus, starting from the *O,N*-acetal, a C_2-unit and a linear or cyclic C_n-unit can be stereospecifically introduced into position 7 of the bicyclo[4.1.0]heptane system.

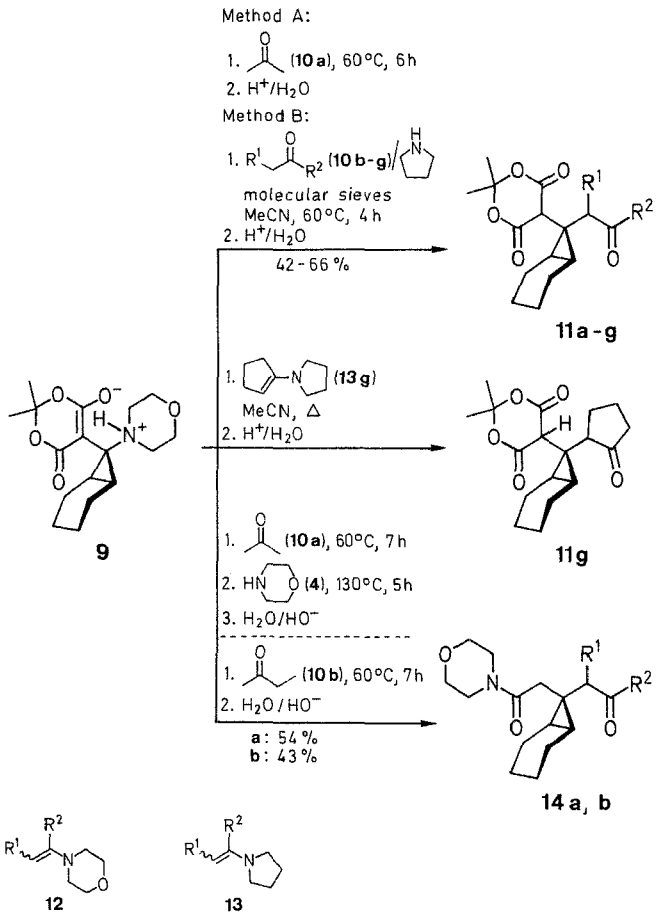
The reaction sequence **1** → **5** → **6** → **2**, which proceeds via cyclopropaniminium ion **7** and (diacylmethylene)cyclopropane **8** as intermediates, represents a promising concept for the twofold nuucleophlic substitution at cycloalkane-fused cyclopropanes.[1-9] Whereas the first nucleophile necessarily is a cyclic 1,3-dioxo compound **3**, a variety of reagents can be used in the second step. If this second step is also to result in C–C bond formation with the cyclopropane, either a *C*-nucleophile or a cycloaddition component is required for trapping **8**.



Cycloaddition reactions of **8** have previously been achieved with a pentadiene and with 2,3-dimethylbutadiene;[7] other trapping agents found to be suitable for monocyclic cyclopropylidene-1,3-cycloalkanediones are enol ethers,[8,9] a 1-alkynyl ether,[9] and an ynamine.[9] A few hitherto described reactions can also be classified as twofold nucleophilic substitutions at a cyclopropane ring with C–C bond formation: These reactions start from cyclopropanone hemiaminals[10] or hemiacetals.[11,12]

Only cyanide ion[6] and rather strongly acidic cyclic 1,3-dicarbonyl compounds[1-5] proved to be suitable *C*-nucleophiles for trapping intermediates **8**: Thus, with dimedone, Meldrum's acid, and other 1,3-cycloalkanediones (pK < 6)[1,2,4] the substitution products **2** could be obtained whereas less acidic compounds such as 2,4-pentanedione (pK_s = 9.0[13]) and dimethyl malonate (pK_s = 13.3[14]) did not undergo the reaction. However, acidity is not the limiting factor for the applicability of a *CH* acid as trapping reagent in the sequence **6** → **2**. This is clearly demonstrated by the reaction of 2,2-dimethyl-5-(7-morpholinobicyclo-[4.1.0]hept-7-yl)-4,6-dioxo-1,3-dioxane **(9)** with various 2-alkanones reported here.

Heating compound **9** in excess acetone **(10a)** gives substitution product **11a** in 66% yield although **10a** (pK_s = 19.1[15]) is distinctly less acidic than 2,4-pentanedione. As a by-product, carboxamide **14a** is obtained in 4% yield; it results from degradation of the Meldrum's acid moiety in **11a** by morpholine formed in the elimination step. This degradation is observed as the main reaction when butanone **(10b)** is used in place of acetone, carboxamide **14b** being isolated in 43% yield. It turned



10–14	R^1	R^2	10–14	R^1	R^2
a	H	CH_3	**e**	H	C_6H_5
b	H	C_2H_5	**f**	H	$CH_2C_6H_5$
c	H	n-C_3H_7	**g**	$-(CH_2)_3-$	
d	H	n-C_4H_9	**h**	CH_3	C_2H_5
			i	H	t-C_4H_9

Table 1. 2,2-Dimethyl-4,6-dioxo-5-[(1α,6α,7β)-7-(2-oxoalkyl)bicyclo[4.1.0]hept-7-yl]-1,3-dioxanes **11** Prepared from Compounds **9** and Ketones **10**

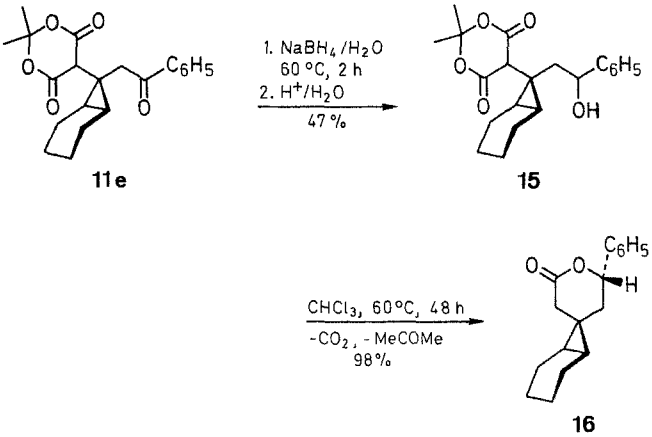
Product	Method	Yield[a] (%)	mp (°C)[b] (solvent)	Molecular Formula[c]	IR (KBr)[d] $\nu_{C=O}$ (cm^{-1})
11a	A	66[e]	82 (MeOH)	$C_{16}H_{22}O_5$ (294.4)	1770, 1738, 1690
11a	B	43			
11b	B	42	92 (dec) (MeOH)	$C_{17}H_{24}O_5$ (308.4)	1775, 1740, 1698
11c	B	63	116 (dec) (Et_2O)	$C_{18}H_{26}O_5$ (322.4)	1768, 1732, 1695
11d	B	59	110 (dec) (Et_2O)	$C_{19}H_{28}O_5$ (336.4)	1775, 1740, 1700
11e	B	63	95 (dec) (Et_2O)	$C_{21}H_{24}O_5$ (356.4)	1775, 1735, 1660
11f	B	43	87 (dec) (MeOH)	$C_{22}H_{26}O_5$ (370.4)	1775, 1740, 1710
11g	B	57	121 (dec) (MeOH)	$C_{18}H_{24}O_5$ (320.4)	1778, 1740, 1720

[a] Yield of isolated product **11** based on **9**.
[b] Uncorrected, measured with a Mettler-FP 61 apparatus.
[c] Satisfactory microanalyses obtained: C ±0.24, H ±0.12; performed with a Perkin-Elmer Elemental Analyzer 240.
[d] Recorded on a Perkin-Elmer IR 397 spectrometer.
[e] In addition, compound **14a** is obtained; yield: 4%; mp 142°C.

out, that the primary product **11b** can be obtained by performing the reaction of **9** with butanone **(10b)** in the presence of pyrrolidine and molecular sieves. Similarly, the 2-oxoalkyl derivatives **11c–f** are obtained from **9** and 2-alkanones **10c–f** under these conditions in 43–63% yields.

Probably an enamine **12** from morpholine and the ketone or an enamine **13** from the ketone **10** and pyrrolidine in the presence of molecular sieves, is the reactive intermediate. This is confirmed by the reactions of **9** with cyclopentanone **(10g)** and with 1-pyrrolidinocyclopentene **(13g)**, both leading to the same product **11g**. Ketones **10b–d** react regiospecifically at the methyl group. Even activation of the methylene group by an adjacent phenyl group does not alter this fact, phenylacetone **(10f)** still reacting with its methyl group due to the steric influence. The sterically induced limitation of the trapping of **8** is demonstrated by heating **9** and 3-pentanone **(10h)** or pinacolone **(10i)** in the presence of pyrrolidine and molecular sieves; neither **10h** nor **10i** reacted to give products of the types **11** or **14**. Cyclopentanone **(10g)** shows less steric hindrance as a consequence of its cyclic structure; this explains the different behavior of **10g** with respect to **10h**.

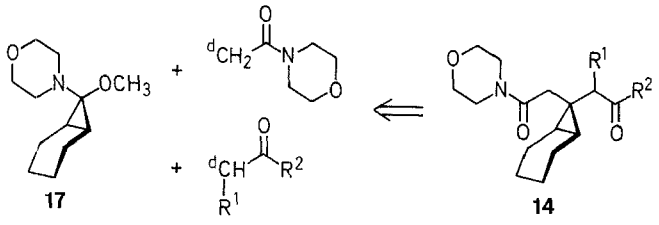
Degradation of the Meldrum's acid moiety in **11** to an aminocarbonyl group by an amine (e.g., morpholine) leads to 7-(2-oxoalkyl)bicyclo[4.1.0]heptane-7-acetamides. This reaction is performed easily with **11b**; in the case of **11a**, heating in the presence of morpholine is necessary. As shown for **11e**, the ketonic carbonyl group can be selectively reduced by sodium borohydride without affecting the Meldrum's acid moiety. The resultant alcohol **15** is not very stable; already at 30–40°C, acetone and carbon dioxide are split off to give lactone **16**.



The bicyclo[4.1.0]heptane structure in all products is clearly established by the ^{13}C-NMR spectra. A singlet at $\delta = 20–24$ and a doublet at $\delta = 17–21$ correspond to the three-membered ring in **11a–g** and **14a, b**. Three instead of two cyclopropane signals in the same range are observed for **11g** and **16** as a consequence of the asymmetry of these compounds. An X-ray structural analysis indicates the 1α,6α,7β structure for **14a**. This information allows the structural assignment of all other derivatives described here: In the ^{13}C-NMR spectra of diastereoisomeric bicycloheptyl-Meldrum's acid derivatives a difference of ~ 10 ppm is observed for the C-5 signals of the Meldrum's acid moiety in the *endo* and *exo* positions.[1,3,5] For compounds **11a–g**, this signal consistently appears at $\delta = 46.0–46.7$ so that the Meldrum's acid moiety is in the same position in all these compounds. Since the degradation **11** → **14**, the reduction **11** → **15**, and the lactone formation **15** → **16** are not accompanied by any change in configuration,[6,16,17] the structures of **11a–g**,

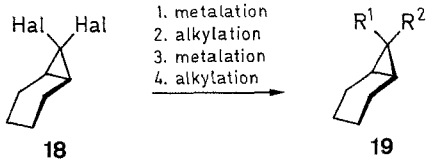
14b, **15**, and **16** also correspond to a 1α, 6α, 7β arrangement. This type of configuration, which is also obtained with other nucleophiles,[1,5-7,17] stems from the strongly preferred attack of the trapping reagent at the sterically less hindered *exo* position of the intermediate **8**.

The interaction of **9** with **10** leads to the introduction of a 2-oxoalkyl group into a norcarane system. This reaction can be used for the stepwise synthesis of compounds **14** from *O,N*-acetal **17**. The overall result corresponds to a stereospecific connection of a $^dC_2$-unit and a linear ^dC_n-unit to a three-membered ring by a (formal) twofold nucleophilic substitution.



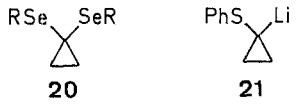
17 **14**

This principle is of wider applicability than the analogous twofold radical process. The latter method allows the connection of only few *C*-nucleophiles (e.g., the anions of acetone or pinacolone) to a three-membered ring by displacement of two Br-atoms in **18**, Hal = Br.[18]



18 **19**

In general, the introduction of two alkyl groups into a cyclopropane starts from the corresponding dibromo derivative and uses a combination of organometallic reagents and alkylating agents.[19-34] This corresponds to an electrophilic substitution at the cyclopropane. It can be utilized for the highly stereoselective synthesis of norcaranes bearing two different alkyl groups at C-7.[20-25,28,29] Diseleno derivatives **20**[35] or sulfur compound **21**[36] can also be used as starting materials for analogous reactions and allow a twofold substitution at a cyclopropane in some cases; at least one step corresponds to an electrophilic exchange.



20 **21**

The twofold nucleophilic substitution starting from *O,N*-acetal **17** and using a ketone as the second nucleophile seems to be a useful supplementation of metalation methods for the introduction of two unbranched *C*-substituents into a norcarane.

2,2-Dimethyl-4,6-dioxo-5-[(1α,6α,7β)-7-(2-oxoalkyl)bicyclo[4.1.0]hept-7-yl]-1,3-dioxanes 11; General Procedures:

Method A (for compound **11a**): A mixture of 2,2-dimethyl-5-(7-morpholinobicyclo[4.1.0]hept-7-yl)-4,6-dioxo-1,3-dioxane[16] (**9**; 1.62 g, 5 mmol) and acetone (**10a**; 30 mL) is stirred at 60 °C for 6 h. Acetone is removed at reduced pressure and the residue is dissolved in aqueous 0.1 M NaOH (50 mL). Degradation product **14a** is obtained by extraction of the alkaline solution with Et_2O (2 × 50 mL). Addition of $NaHSO_4$ to the aqueous solution till pH 1 gives product **11a** as a colorless precipitate; it is extracted from the mixture with Et_2O (2 × 50 mL). The crude products **11a** and **14a**, which remain after evaporation of their Et_2O solutions, are recrystallized from Et_2O.

Table 2. NMR-Spectrometric Data[a] of Compounds **11**

Compound	^{1}H-NMR ($CDCl_3$/TMS) δ			^{13}C-NMR ($CDCl_3$/TMS) δ							
	Meldrum's Acid Moiety		Further Signals	Meldrum's Acid Moiety				Bicyclic System			Further Signals
	CH_3 (s)	5-H (s)		CH_3 (q)	C-5 (d)	C-2 (s)	C-4 C-6 (s)	C-7 (s)	C-1 C-6 (d)[b]	C-2–C-5 (t)	
11a	1.75, 1.83	3.26	0.93–1.56 (m, 6H); 1.11–1.20 (m, 2H); 1.96–2.13 (m, 2H); 2.16 (s, 3H); 2.41 (s, 2H)	27.1, 28.4	46.1	104.9	164.7	23.4	20.5	19.7, 22.5	32.1 (q), 49.6 (t), 210.1 (s)
11b	1.75, 1.85	3.25	0.9–1.11 (m, 2H); 0.96 (t, 3H); 1.11–1.22 (m, 2H); 1.28–1.55 (m, 4H); 1.94–2.19 (m, 2H); 2.37 (s, 2H); 2.49 (q, 2H)	27.1, 28.4	46.2	104.8	164.5	23.6	20.4	19.7, 22.4	7.3 (q), 37.9 (t), 48.4 (t), 212.0 (s)
11c	1.75, 1.85	3.24	0.88 (t, 3H); 0.96–1.26 (m, 4H); 1.29–1.64 (m, 6H); 1.96–2.20 (m, 2H); 2.38 (s, 2H); 2.42 (t, 2H)	27.1, 28.4	46.1	104.6	164.3	23.5	20.5	19.7, 22.5	13.6 (q), 16.8 (t), 46.8 (t), 48.5 (t), 211.3 (s)
11d	1.75, 1.85	3.24	0.88 (t, 3H); 0.95–1.57 (m, 12H); 1.95–2.21 (m, 2H); 2.38 (s, 2H); 2.43 (t, 2H)	27.1, 28.5	46.1	104.6	164.3	23.5	20.5	19.7, 22.5	13.9 (q), 22.2 (t), 25.5 (t), 44.6 (t), 48.5 (t), 211.4 (s)
11e	1.77, 1.84	3.36	0.9–1.55 (m, 8H); 1.91–2.21 (m, 2H); 2.98 (s, 2H); 7.35–7.65 (m, 3H); 7.9 (d, 2H)	27.1, 28.4	46.7	104.8	164.6	23.8	19.7	19.6, 22.5	42.6 (t), 128.8 (d), 133.4 (d), 138.0 (s), 200.8 (s)
11f	1.73, 1.81	3.26	0.9–1.18 (m, 4H); 1.25–1.56 (m, 4H); 1.93–2.16 (m, 2H); 2.36 (s, 2H); 3.73 (s, 2H); 7.10–7.36 (m, 5H)	26.9, 28.3	46.0	104.8	164.5	23.5	20.3	19.6, 22.4	47.3 (t), 51.6 (t), 127.1 (d), 128.8 (d), 130.0 (d), 134.1 (s), 209.0 (s)
11g	1.78, 1.88	3.23	0.9–2.24 (m, 16H); 2.63 (t, 1H)	27.1, 28.6	46.3	104.6	164.7, 165.1	24.3	18.4, 17.7	19.8, 22.6	18.7 (t), 20.5 (t), 27.6 (t), 39.3 (t), 49.8 (d), 220.4 (s)

[a] Recorded on a Bruker WP 200 spectrometer at 20 °C.

[b] $^1J_{^1H^{13}C}$ = 156–165 Hz.

Method B (for compounds **11b–g**): 2,2-Dimethyl-5-(7-morpholinobicyclo[4.1.0]hept-7-yl)-4,6-dioxo-1,3-dioxane[16] (**9**; 1.62 g, 5 mmol) and molecular sieves 3 Å (2 g) are added to a solution of the ketone **10** (25 mmol) and pyrrolidine (2.49 g, 35 mmol) in MeCN (50 mL), and the mixture is stirred at 60 °C for 4 h. An insoluble residue, which is still present at this time, is removed by suction and washed with MeCN (20 mL). The combined MeCN solution is evaporated at reduced pressure, the residue is dissolved in aqueous 0.2 M NaOH (50 mL), and this solution is worked up as in Method A.

2,2-Dimethyl-4,6-dioxo-5-[(1α,6α,7β)-(2-oxocyclopentyl)bicyclo[4.1.0]-hept-7-yl]-1,3-dioxane (11g) from 9 and Enamine 13g:

Compound **9**[16] (1.62 g, 5 mmol) is added to a solution of 1-pyrrolidinocyclopentene[37] (**13g**; 0.82 g, 6 mmol) in MeCN (30 mL); the mixture is stirred for 2 h at 60 °C. The solvent is then removed at reduced pressure and aqueous 0.1 M NaOH (100 mL) is added to the residue. This mixture is washed with Et_2O (3 × 50 mL) and $NaHSO_4$ is added till pH 1. Extraction with Et_2O (2 × 50 mL), evaporation of the extract under reduced pressure, and trituration of the residue with MeOH (~ 10 mL) gives **11g**; yield: 0.7 g (44%); mp 121 °C.

$C_{18}H_{24}O_5$	calc.	C 67.48	H 7.55
(320.4)	found	67.5	7.51

(1α,6α,7β)-7-(2-Oxoalkyl)bicyclo[4.1.0]heptane-7-acetic Acid Morpholides 14a, b; General Procedure:

A mixture of compound **9**[16] (1.62 g, 5 mmol) and ketone **10a, b** (30 mL) is stirred at 60 °C for 7 h. Then the ketone is removed *in vacuo*. In the case of **11b** degradation is complete at this point; for complete degradation of **11a**, the residue thus obtained is heated together with morpholine (**4**; 1 mL, 11.5 mmol) at 130 °C for 5 h, then allowed to stand at 20 °C for 12 h. Excess **4** is removed *in vacuo* and aqueous 0.1 M NaOH (50 mL) is added to the crude degradation products. Extraction with Et_2O (2 × 50 mL), evaporation of the extract, and trituration of the residue with ice-cold Et_2O (2 × 2 mL) gives pure **14a** or **14b**, respectively.

7-(2-Oxopropyl) Derivative **14a**; yield: 0.76 g (54%); mp 142 °C.

$C_{16}H_{25}NO_3$	calc.	C 68.80	H 9.02	N 5.01
(279.4)	found	68.7	9.00	5.1

IR (KBr): ν = 1700, 1635 (C=O) cm^{-1}.

^{1}H-NMR ($CDCl_3$): δ = 0.7–0.87 (m, 2H); 1.0–1.49 (m, 6H); 1.8–2.09 (m, 2H); 2.06 (s, 3H); 2.50 (s, 2H); 2.55 (s, 2H); 3.36–3.54 (m, 2H); 3.54–3.79 (m, 6H).

^{13}C-NMR ($CDCl_3$): δ = 18.7 (d), 19.2 (t), 20.6 (s), 22.2 (t), 29.8 (t), 30.6 (q), 41.9 (t), 46.1 (t), 53.6 (t), 66.8 (t), 67.1 (t), 170.9 (s), 209.6 (s).

7-(2-Oxobutyl) Derivative **14b**; yield: 0.63 g (43%); mp 108–109 °C.

$C_{17}H_{27}NO_3$	calc.	C 69.59	H 9.28	N 4.77
(293.4)	found	69.6	9.18	4.8

IR (KBr): ν = 1695, 1635 (C=O) cm^{-1}.

^{1}H-NMR ($CDCl_3$): δ = 0.70–0.86 (m, 2H); 1.0 (t, 3H); 1.05–1.5 (m, 6H); 1.8–2.05 (m, 2H); 2.35 (q, 2H); 2.52 (s, 4H); 3.39–3.55 (m, 2H); 3.55–3.75 (m, 6H).

^{13}C-NMR ($CDCl_3$): δ = 7.4 (q), 18.4 (d), 19.0 (t), 20.4 (s), 22.0 (t), 29.7 (t), 36.1 (t), 41.6 (t), 45.9 (t), 52.0 (t), 66.6 (t), 66.8 (t), 170.7 (s), 212.0 (s).

5-[(1α,6α,7β)-7-(2-Hydroxy-2-phenylethyl)-bicyclo[4.1.0]hept-7-yl]-2,2-dimethyl-4,6-dioxo-1,3-dioxane (15):

Phenacyl derivative **11e** (1.78 g, 5 mmol) and $NaBH_4$ (1.89 g, 50 mmol) are stirred in H_2O (100 mL) at 60 °C for 2 h. Then, $NaHSO_4$ is at 0 °C added to the mixture till pH 1. Extraction with Et_2O (2 × 50 mL), evaporation of the extract, and trituration of the residue with MeOH (10 mL) gives **15** as a colorless solid; yield: 0.84 g (47%); decomposition already at 30–40 °C.

$C_{21}H_{26}O_5$	calc.	C 70.37	H 7.31
(358.4)	found	70.3	7.21

IR (KBr): ν = 3490 (OH); 1775, 1735 (C=O) cm^{-1}.

^{1}H-NMR ($CDCl_3$): δ = 0.88–1.27 (m), 1.0 (H^1) (together 5H); 1.27–1.53 (m, 3H); 1.53–1.83 (m, 1H); 1.76 (s, 6H); 1.96–2.20 (m, 3H); 2.38 (H^B, 1H, J_{AB} = 15.1 Hz, J_{BX} = 11.0 Hz), 4.84 (H^X, 1H, J_{XB} = 11.0 Hz, ABX system with H^A and H^B); 7.20–7.27 (m, 5H).

(1α,6α,7β)-2′-Oxo-6′-phenyl-2′,3′,5′,6′-tetrahydrospiro[bicyclo[4.1.0]-heptan-7,4′-[4*H*]pyran] (16):

A solution of hydroxy compound **15** (1.79 g, 5 mmol) in $CHCl_3$ (50 mL) is heated at 60 °C for 48 h. Evaporation of the solvent and distillation of the residue in a Kugelrohr apparatus at 250 °C/0.001 mbar gives pure **16**; yield: 1.25 g (98%); mp 67 °C.

$C_{17}H_{20}O_2$	calc.	C 79.65	H 7.86
(256.3)	found	79.6	7.85

IR (KBr): ν = 1715 (C=O) cm^{-1}.

^{1}H-NMR ($CDCl_3$): δ = 0.70–0.95 (m, 2H); 1.0–1.50 (m), 1.39 (H^A) (together 7H); 1.69–2.05 (m, 2H); 2.13 (H^B), (1H, J_{AB} = 14.0 Hz); 2.52 (H^c), 2.64 (H^D), (2H, AB System, J_{CD} = 20.1 Hz); 5.42 (H^X) (1H), ABX System with H^A and H^B, J_{XA} = 2.7 Hz, J_{XB} = 10.8 Hz); 7.22–7.42 (m, 5H).

^{13}C-NMR ($CDCl_3$): δ = 18.2 (t), 18.4 (d), 18.87 (d), 18.94 (t), 19.6 (s), 21.6 (t), 21.8 (t), 30.6 (t), 43.5 (t), 80.6 (d), 125.7 (d), 128.1 (d), 128.5 (d), 139.5 (s), 171.5 (s).

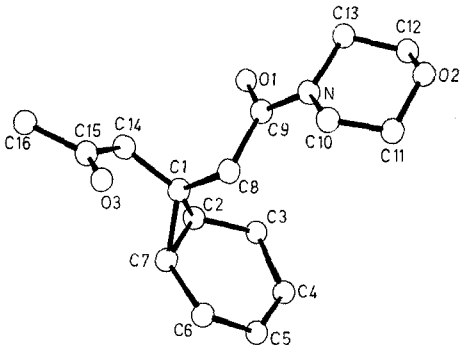


Figure. Molecule plot of (1α, 6α, 7β)-7-(2-Oxopropyl)bicyclo[4.1.0] heptan-7-acetic Acid Morpholid **(14a)**

Table 3. Selected Bond Distances and Bond Angles of (1α,6α,7β)-7-(2-Oxopropyl)bicyclo[4.1.0]heptane-7-acetic Acid Morpholide **(14a)**

Atom 1	Atom 2	Distance[a] (Å)	Atom 1	Atom 2	Atom 3	Angle[a] (Degree)
C1	C2	1.509(7)	C1	C2	C7	60.0(3)
C1	C7	1.511(7)	C1	C7	C2	59.9(3)
C2	C7	1.513(7)	C2	C1	C7	60.2(3)
C2	C3	1.512(8)	C2	C1	C8	119.9(4)
C3	C4	1.500(9)	C2	C1	C14	115.6(4)
C4	C5	1.304(9)	C7	C1	C8	120.3(4)
C5	C6	1.501(9)	C7	C1	C14	115.2(4)
C6	C7	1.517(8)	C8	C1	C14	114.9(4)
C1	C8	1.506(6)				
C1	C14	1.513(7)				

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

X-Ray Structural Analysis of 14a:

Crystal Data: Triclinic space group $P\bar{1}$; unit cell a = 9.613 (2), b = 10.345 (3), c = 8.993 (2) Å; α = 99.77 (2)°, β = 109.25 (2)°, γ = 107.92 (2)°; D_{calc} = 1.21 g · cm^{-3}; Z = 2.

Data Collection: Crystal size 0.4 × 0.3 × 0.3 mm; Enraf-Nonius CAD4 diffractometer; monochromatic Mo K_α irradiation; 2252 independent reflections in the range $2.00 \leq \theta \leq 23.50°$ were measured; scan width $(0.85 + 0.35 \tan\theta)°$; $\theta/2\,\theta$ scan.

Structure Resolution and Refinement: The phase problem was solved using Multan 82. Refinement was performed by a Full-matrix-Least-squares program. Only mean positions are obtained for C-4 and C-5 as a consequence of a disorder of these carbon atoms which simulates an sp^2 hybridization (C-4 – C-5 bond: 1.30 Å); the hydrogen atoms at C-4 and C-5 were ignored; the full matrix refinement with 1822 reflections [$I > 2\,\sigma$ (I)] and unit weights converged at R = 0.075, $R_w = (\Sigma\Delta^2 F_0/\Sigma F_0^2)^{1/2} = 0.071$. The largest shift/error ratio at this stage was less than 0.01. Tables of positional and thermal parameters, the list of bond lengths and angles, and a list of the observed and calculated structural factors have been deposited.[38]

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(38) Further information on the X-ray analysis of **14a** is available from: Fachinformationszentrum Energie, Physik, Mathematik, D-7514 Eggenstein-Leopoldshafen. Requests should indicate the depository number CSD 52934, the names of the authors, and the literature citation of this paper.