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THE CLEMMENSEN REDUCTION OF PENTACYCLO[6.4.0.0^{2,7}.0^{3,11}.0^{6,10}]DODECANE-9,12-DIONE

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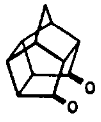
Abstract - The Clemmensen reduction of pentacyclo[6.4.0.0^{2,7}.0^{3,11}.0^{6,10}]dodecane-9,12-dione unexpectedly led to the formation of pentacyclo[6.4.0.0^{2,6}.0^{5,9}.0^{4,12}]-2-dodecanol and pentacyclo[6.4.0.0^{2,7}.0^{3,11}.0^{6,10}]dodecane-1,8-diol as main products. Tetracyclo[6.4.0.0^{5,9}.0^{4,12}]dodecane-2,7-dione and its corresponding hemiacetal were obtained as byproducts. The structures of the Clemmensen products were elucidated from an extensive ^{1}H and ^{13}C n.m.r. study.

The reduction of ketones to the corresponding alkanes using amalgamated zinc and hydrochloric acid has been widely employed in organic synthesis. The reduction of difunctional ketones under Clemmensen conditions, while often of synthetic importance, rarely yields the expected alkanes in acceptable yield. The reduction of 1,4-diketones is of considerable interest in that it leads to many unexpected and usually inaccessible compounds. The product variety and distribution depends on both the conformation and electronic environment of the carbonyl groups.[1]

It is well known that treatment of 1,2-dicarbonyl substituted cyclobutane derivatives with zinc in acidic medium leads to reductive cyclobutane ring cleavage.[1,2,3] *Syn*- or *anti*-periplanar alignment of the carbonyl groups with the C_2-C_3-bond of a cyclic 1,4-diketone favours ring cleavage.[1] When interaction of the carbonyl groups is possible cyclobutane diols can be formed.[1] Accordingly Wenkert and Yoder[3] found that treatment of pentacyclo[5.4.0.0^{2,6}.0^{3,10}.0^{5,9}]undecane-8,11-dione (1) with zinc and acetic acid leads to the tetracyclic diketone 2, which, on further treatment with amalgamated zinc and hydrochloric acid, is reduced to the pinacol 3. As expected both 2 and 3 were isolated[4] from the Clemmensen reduction of 1.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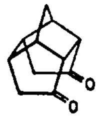
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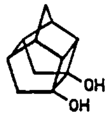
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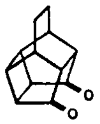
It was previously reported[4] that 1 and its homologue 4 (pentacyclo[6.4.0.0^{2,7}.0^{3,11}.0^{6,10}]dodecane-9,12-dione)[5] behave differently towards nucleophiles, owing to a smaller intercarbonylic distance in the latter case. This suggests that the Clemmensen reduction of 4 can also take a different course.

It was shown[6,7] that treatment of 4 with zinc powder in acetic acid produces the hemiacetal 5 in high yield. We found that the reaction of 4 with amalgamated zinc and hydrochloric acid (6 mol dm^{-3}) took a remarkable different course, leading mainly to the pinacol 6 (30%) and the alcohol 7 (45%) while small quantities of 8 (15%) and 9 (10%) have also been formed.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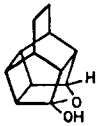
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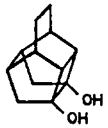
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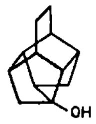
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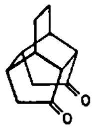
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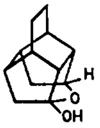
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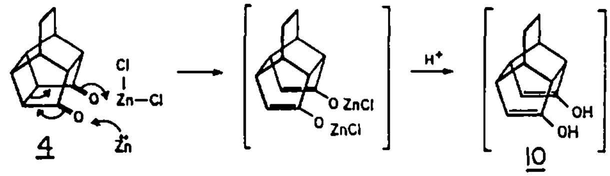
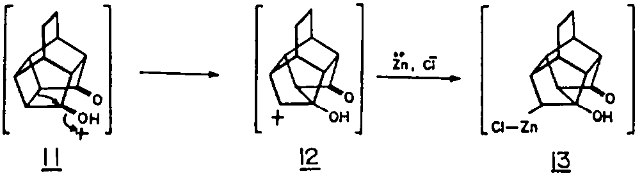
To gain more information on the reactions involved in the reduction of 4 with amalgamated zinc and hydrochloric acid, 4 was subjected to treatment with zinc powder and hydrochloric acid. No alcohol 7 was formed at all while 6, 8 and 9 were obtained in the ratio 6:3:2 respectively. This result suggested that 8 is the precursor for the formation of 6 and 9 in the Clemmensen reduction of 4 and that the formation of 7 is dependent on the acid concentration since the hydrogen ion concentration rapidly decreases under these reaction conditions. Treatment of 8 with amalgamated zinc and hydrochloric acid indeed resulted in the formation of 6 and 9. It is obvious that two competing reactions are involved in the Clemmensen reduction of 4 and that 7 and 8 are probably formed as primary products.

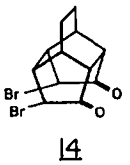
Both zinc and zinc chloride play an essential role in the cleavage of 1,2-dicarbonyl substituted cyclopropane and cyclobutane compounds.[2,8] Two sites are available for an initial metal substrate attack, namely the carbonyl oxygen and the carbonyl carbon atoms. An initial zinc-oxygen attack is thought more probable for difunctional ketones[1] whereby 8 can be obtained via the intermediate enol form 10.



As expected the yield of 7 was increased to 60% when 4 was subjected to a Clemmensen reduction at increased acid concentration (11 mol dm^{-3}). Under these reaction conditions protonation of a carbonyl group will probably dominate zinc-zinc chloride attact on the carbonyl groups. The protonated species 11 can release its ring strain via rearrangement whereby the carbocation 12 is formed. Zinc attack on the positively charged carbon atom in 12 followed by normal Clemmensen reduction of 13 leads to the formation of 7.



The presence of two hydroxyl groups in 6 was proved by its conversion to the corresponding diacetate. The structural relationship between 6 and 8 was demonstrated by treatment of 6 with aqueous sodium periodate whereby 8 was obtained. Treatment of 8 with magnesium and magnesium iodide, according to the procedure of Gomberg and Bachmann,[9] led to the formation of 6. Further proof for the correctness of the structure of 8 was obtained through conversion to the dibromide 14 which gave 4 upon pyrolysis with copper powder. The dibromide 14 also suffered reductive dehalogenation when treated with zinc powder in ethanol to give 8.



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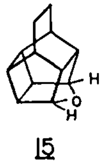

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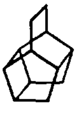

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The Clemmensen product 9 was completely identical to the hemiacetal obtained[7] from the lithium aluminium hydride reduction of 8. The structure of the hemiacetal (9) was previously assigned[7] only from infrared, mass spectrometrical data and conversion to a mono acetate. Confirmatory evidence for the correctness of the structure of 9 was obtained from a ^1H and ^{13}C n.m.r. study which clearly reveals its asymmetrical character. The n.m.r. data of 9 are given in Table 1.

^1H and ^{13}C n.m.r. spectroscopy should be the methods of choice for the elucidation of the structures of these types of compounds. However, their ^1H n.m.r. spectra, even at

500 MHz, are very complex. Only from a few proton resonances can proton-proton coupling constants be obtained. In addition to geminal and vicinal proton-proton couplings, long range (over more than three bonds) proton-proton interactions are also operative, resulting in fairly broad unresolved resonances. The tables in which the ^{1}H n.m.r. data have been collected only give those splittings that could be measured and the few, mostly geminal, coupling constants that could be assigned.

The ^{13}C n.m.r. spectrum of 9 exhibits the presence of one quaternary carbon atom (C-1) at δ 116.15. The chemical shift of C-1 is indicative of the presence of two neighbouring electronegative groups. The presence of seven methine and four methylene carbon atoms in 9 are also clearly displayed in the ^{13}C n.m.r. spectrum. The ^{1}H n.m.r. spectrum of 9 exhibits signals from an ABCD part of an ABCDXY spin system attributable to the two methylene groups associated with C-4 and C-5. The remaining two methylene groups at C-9 and C-12 exhibit geminal coupling constants characteristic of those observed for normal five or six membered rings. Only one of these methylene protons (H_b-9) coupled appreciable to other protons, probably to H-8 and H-10. The allocation of signals to certain protons was supported by a ^{1}H COSY experiment. The ^{13}C signals were assigned with a HETCOR experiment from the assigned proton spectrum.

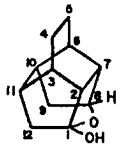
Table 1 ^{1}H and ^{13}C n.m.r. data[a] of 9

Carbon/ proton	^{1}H δ(ppm)	J(Hz)			^{13}C δ(ppm)[b]	^1J(Hz)
1					116.15 S	
2	2.058 m				38.13 D	142.0
3	1.750 m(br)				35.24 D	134.6
4a	ABCD[c]				18.63 T*	128.6
4b						
5a					18.90 T*	130.0
5b						
6	1.380 m(br)				37.31 D	132.3
7	2.471 dddd	10.4 4.1	6.2 2.0		45.64 D	142.2
8	4.658 dd	6.9	6.2		80.33 D	156.1
9a	1.827 d	13.8(9a,b)			38.31 T	132.4
9b	1.435 ddd	6.9	4.6			
10	2.036 m				38.10 D	143.0
11	1.920 ddd	10.6	4.1	2.8	51.28 D	142.2
12a	2.071 d	13.4(12a,b)			44.36 T	130.8
12b	1.639 d					
OH	3.603 S(br)					

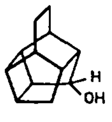
[a] ^{1}H:500 MHz; ^{13}C:125 MHz. Solvent $CDCl_3$. Chemical shifts relative to TMS. The numbers in brackets give the coupling protons if known.

[b] Values marked * are mutually interchangeable.

[c] ABCD part of an ABCDXY spin system with one proton centered around δ 1.550 and three protons around δ 1.147.



The infrared spectrum of the Clemmensen product 7 exhibits a strong O-H stretching vibration absorption at 3 224 cm^{-1}. Acetylation of 7 with acetic anhydride containing sodium acetate produced a mono-acetate. The mass spectrum of 7 shows a molecular ion at m/z 176 which fragments to an ion at m/z 158 corresponding to a loss of one molecule of water. An elemental analysis indicated a molecular composition of $C_{12}H_{16}O$. Four possible structures (7, 17, 18 and 19) could be deduced from the above data. In order to obtain more information on the structure of the mono-alcohol an extensive ^1H and ^{13}C n.m.r. study was conducted. The n.m.r. data of 7 are given in Table 2.



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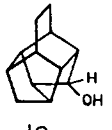

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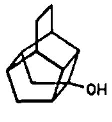

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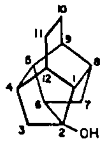
The ^1H n.m.r. spectrum of 7 is very complex and consists of two groups of signals, one around δ 2.1 (representing three protons) and the other from δ 1.1 to δ 1.8 (accounting for thirteen protons). At the high field region of the latter multiplet two doublets, representing parts of two AB spin systems and therefore two independent methylene groups, are visible.

Structures 17 and 18 can be ruled out immediately as possibilities for the mono-alcohol because of the absence of a proton resonance in the δ 3.5-4.0 region where protons which are bonded to a carbon atom bearing a hydroxyl groups should resonate. Support for the conclusion that 7 does not contain a secondary hydroxyl group is rendered by the quaternary carbon resonance observed at δ 88.96, indicating a tertiary alcohol.

Table 2 ^1H and ^{13}C n.m.r. data[a] of 7

Carbon/ proton	^1H δ(ppm)	^1H J(Hz)	Δ^b_{Eu}(ppm)	^{13}C δ(ppm)	^{13}C J(C,H)(Hz)	Δ^c_{Yb}(ppm)
1	1.8		1.00	46.87 D	139.4	1.00
2	1.7(OH)			88.96 S		2.31
3a	1.5	2.2	0.91	40.42 T	132.8	1.06
3b	1.3	9.0(3a,b)	0.95			
4	1.8		0.39	35.49 D	139.6	0.52
5	2.0	6.0	0.40	39.69 D	145.0	0.51
6	2.1	6.0	0.97	51.22 D	144.2	1.01
7a	1.8		1.02	32.27 T	132.9	0.71
7b	1.1	9.8(7a,b)	0.49			
8	2.1	4.8	0.42	38.72 D	139.0	0.58
9	1.7		0.23	37.89 D	133.2	0.37
10	1.5		0.23	18.80 T	126.0	0.19
11	1.5		0.23	18.70 T	126.0	0.24
12	1.7		0.45	39.30 D	133.0	0.44



[a] ^1H:90 MHz; ^{13}C:20 MHz. Solvent $CDCl_3$. Chemical shifts relative to TMS. The numbers in brackets give the coupling protons if known.

[b] $Eu(fod)_3$ induced shift of H-1 taken as one.

[c] $Yb(fod)_3$ induced shift of C-1 taken as one.

The structure of 6 was unambiguously determined from a X-ray diffraction study[10] and should be a good comparative model compound for the structure of 19. A distinctive feature of the ^1H n.m.r. spectrum of 6 (Table 3) is the presence of an AB spin system with a geminal coupling of 11.4 Hz. The low field half is a sharp doublet (δ 1.90) while the high field doublet (δ 1.17) exhibits triplet-like broadening with an apparent coupling of 1.4 Hz. In agreement with the appearance of "AB quartets" observed for corresponding methylene groups in related cage compounds,[11] the sharp doublet was assigned to the *endo* protons (H_a-9 and H_a-12) of carbons 9 and 12, and the broad signals to the *exo* protons H_b-9 and H_b-12. The hydroxyl protons resonate at δ 3.13. As a consequence of the symmetry of 6 only four other absorptions at δ 1.60, 1.63, 2.20 and 2.27 were registered. From a model calculated by the MM2 force field program[12] the distances between the different nuclei in 6 and the europium atom of the shift reagent $Eu(fod)_3$-d_{30} could be calculated. Using the known interatomic distance dependence of observed lanthanide induced shifts the four signals were assigned to H-3 (H-6), H-4 (H-5), H-10 (H-11) and H-2 (H-7) respectively. Decoupling of H-2 (H-7) in a $Eu(fod)_3$-d_{30} induced shifted ^1H n.m.r. spectrum confirmed the assignment of H-3 (H-6). The ^1H n.m.r. data of 6 indicate that 19 is probably not the correct structure for the mono-alcohol.

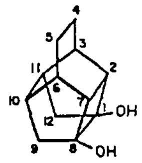
Table 3 ^1H and ^{13}C n.m.r. data[a] of 6

Carbon/ proton	^1H δ(ppm)	^1H J(Hz)	^1H Δ^b_{Eu}(ppm)	^{13}C δ(ppm)	^{13}C J(C,H)(Hz)	^{13}C Δ^c_{Yb}(ppm)
1(8)	3.13(OH)		4.38	82.8 S		2.44
2(7)	2.27	1.8(2,3)	1.00	43.1 D	145	1.00
3(6)	1.60		0.68	34.5 Dd	134.3 ; 9.4	0.52
4(5)	1.63		0.28	19.2 T	129.8	0.28
9a(12a)	1.90	11.4(9a,b)	0.98	34.2 T	131.3	0.88
9b(12b)	1.17	1.4(9,10)	0.98			
10(11)	2.20		0.47	36.8 D	134	0.53

[a] ^1H:90 MHz; ^{13}C:20 MHz. Solvent $CDCl_3$. Chemical shifts relative to TMS. The numbers in brackets give the coupling protons if known.

[b] $Eu(fod)_3$ induced shift of H-7 taken as one.

[c] $Yb(fod)_3$ induced shift of C-2 taken as one.



In order to discriminate between 7 and 19 the correlation between interatomic distances and lanthanide induced shifts on the n.m.r. resonances were used. X-ray crystallographic data of 6[10] and 15[13] correlate well with the molecular geometries obtained with the MM2 force field calculations. The relative strain energies of 4, 7 and 19 obtained with the MM2 force field calculations[12] are 232.56, 182.84 and 245.45 kJ respectively. The substantial higher calculated relative strain energy of 19 compared to 4 is an indication that it is highly improbable that 19 represents the structure of the mono-alcohol. The relative strain energy of 7 is considerably lower than that of 4.

As expected, a marked difference in the lanthanide induced shifts of the methylene protons on C-3 and C-7 were found. H_a-3 (δ 1.7) and H_b-3 (δ 1.3) exhibited almost identical shifts, whereas H_a-7 (δ 1.6) shifted even faster, almost twice as fast as H_b-7 (δ 1.1). These lanthanide induced shifts can only be explained for 7.

The assignments given in Table 2 were confirmed by decoupling experiments on shifted spectra. The H-3a signal showed an additional coupling of 2 Hz which disappeared when H-4 was irradiated. Decoupling of H-12 led to a sharpening of the H-1 signal. The 6 Hz coupling of H-5 disappeared on irradiation of H-6. Simultaneous decoupling of H-7a and H-1 led to a sharpening of the signal assigned to H-12 as well as the removal of the 4.8 Hz coupling of H-8. A further decoupling experiment indicated a relation between H-8 and the protons H-9 and H-1. The relationship between H-9 and H-8 was confirmed by the reverse irradiation of H-9. The latter experiment also affected H-5. This then confirmed the relation between the protons 4-3, 7-8 and 6-5-9-8-1-12. It was not possible to confirm the coupling between H-5 and H-4 by decoupling experiments because of the small chemical shift difference in shifted spectra.

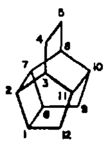
The assignment of the different resonance signals in the ^{1}H n.m.r. spectra of 6 and 7 to certain nuclei was verified by comparison to the n.m.r. data of 16 (Table 4). The hydrocarbon 16 was obtained from a Huang-Minlon[14] reduction of the diketone 4. Characteristically the protons on carbon 9(12) of 16 appear as an AB spin system [δ(H_b-9) = 0.82 and δ(H_a-9) = 1.74]. As previously described (^{1}H n.m.r. of 6) the sharp doublet at δ 1.74 can be attributed to the *endo* protons on C-9 and C-12. The assignment, as summarised in Table 4, was confirmed by decoupling experiments in deuterio benzene. Decoupling of the broadened doublet at δ 0.82 affected the signals at δ 2.68 and 2.20 [H-1 (H-8) and H-10 (H-11)]. Irradiation at δ 1.25 influenced the signals at δ 2.49 and 2.20 as well as the AA'BB' system at δ 1.68. Obviously the latter is the resonance position of the protons on C-4 and C-5. The irradiated proton(s) must then be H-3 (H-6), H-10 (H-11) resonates at δ 2.20 and the signals at δ 2.68 and 2.49 correspond to the resonances of H-1 (H-8) and H-2 (H-7) respectively.

Table 4 ^{1}H and ^{13}C n.m.r. data[a] of 16

Carbon/ proton	^{1}H δ(ppm)	^{1}H J(Hz)	^{13}C δ(ppm)	^{13}C J(C,H)(Hz)
1(8)	2.68		37.5 D	134
2(7)	2.49		38.7 D	147
3(6)	1.25		35.2 Dd	133 ; 9.0
4(5)	1.68[b]		19.4 Td	128 ; 4.8
9a(12a)	1.74	11.4(9a,b)	27.5 T	128.3
9b(12b)	0.82			131.0
10(11)	2.20		37.9 D	133

[a] ^{1}H:90 MHz; ^{13}C:20 MHz. Solvent $CDCl_3$. Chemical shifts relative to TMS. The numbers in brackets give the coupling protons if known.

[b] Centre of AA'BB' spin system.



The ^{13}C n.m.r. spectrum of 6 (Table 3) exhibits six different signals: a signal from the carbon atom C-1 (C-8) at δ 82.8, signals from the methylene carbon atoms C-4 (C-5) and C-9 (C-12) at δ 19.2 and 34.2, two signals from the methine carbon atoms C-2 (C-7) and C-10 (C-11) at δ 43.1 and 36.8 respectively and a striking doublet of doublets at δ 34.5 which can be attributed to C-3 (C-6). The dihedral angle of 177° (obtained from force field calculations) between C-3 (C-6) and H_a-12 (H_a-9) sufficiently explains the coupling of 9.4 Hz. Lanthanide induced shifts supported the assignment of the signals. The signal at δ 43.1 shifted fastest after the singlet arising from C-1, thus assigning it to C-2 (C-7). Appreciable shifts were also observed for the signal at δ 34.2 supporting the assignment to C-9 (C-12). The lanthanide induced shifts of the signals at δ 34.5 and 36.8 were very similar and were assigned to C-3 (C-6) and C-10 (C-11) respectively by selective population inversion experiments.[15] The C-4 (C-5) signal showed, as expected, the smallest shift.

The ^{13}C n.m.r. spectrum of 7 (Table 2) exhibits signals that can be associated with twelve different carbon atoms. The carbon atom C-2 resonates at δ 88.9. Methylene carbon atoms resonate at δ 40.4, 32.3, 18.8 and 18.7 and were assigned to C-3, C-7, C-10 and C-11 respectively using lanthanide induced shifts. An off-resonance proton decoupled ^{13}C n.m.r. experiment on a Yb(fod)$_3$-shifted sample indicated that the methine carbon atoms C-1, C-6 and C-9 resonate at δ 46.9, 51.2 and 37.9 respectively. Off-resonance experiments also indicated that the hydrogen atoms which are directly bonded to the carbon atoms resonating at δ 39.7 (C-5) and 38.7 (C-8), appear in the ^1H n.m.r. spectrum at lower field than the ones directly bonded to the carbon atoms resonating at δ 35.5 (C-4) and 39.3 (C-12). The C-12 signal could be distinguished from the signal associated with C-4 by comparison of the directly bonded (C,H) coupling constant [$^1J(C,H)$ = 133 Hz] with the corresponding values obtained for 6 and 16 (134.3 and 133 Hz respectively). C-5 and C-8 were assigned from lanthanide induced shift experiments.

Six different resonances are registered in the ^{13}C n.m.r. spectrum of the hydrocarbon 16 (Table 4). The methylene carbon atoms C-9 (C-12) and C-4 (C-5) resonate at δ 27.5 and 19.4 respectively. The characteristic doublet of doublets obtained for C-3 (C-6) in 6 also appears in this spectrum. The remaining methine carbon atoms resonate at δ 38.7, 37.5 and 37.9 and were assigned to C-2 (C-7), C-1 (C-8) and C-10 (C-11) respectively by off-resonance proton decoupled experiments. Directly bonded (C,H) coupling constants were determined from selective population inversion experiments[15] and are also given in Table 4.

EXPERIMENTAL

Infrared spectra (KBr-disc) were recorded on a Nicolet 5 DX FT-spectrophotometer. Mass spectra were obtained at 70 eV on a VG 70-70 E mass spectrometer. Melting points are uncorrected. Elemental analyses were performed on a Hewlett-Packard analyser. The ^1H and ^{13}C n.m.r. spectra were recorded on a varian EM 390, a Bruker WM 500 FT and a Varian CFT 20 spectrometer as indicated.

Clemmensen Reduction of 4

A mixture of 4 (4 g), zinc amalgam (40 g), 6 mol dm^{-3} hydrochloric acid (70 cm^3) and methanol (10 cm^3) was boiled under reflux for 1 h. Steam distillation of the reaction mixture produced 7 (1.53 g, m.p. 141-143°C) as the sole product in the distillate. The residue was cooled, neutralised with sodium bicarbonate and the organic phase extracted with dichloromethane. Flash chromatography[16] with silica gel (E. Merck Kieselgel 60; 38-63 µm) as stationary phase and a 1:1:1 mixture of benzene, diethyl ether and ethyl acetate as eluant produced 9 (0.34 g, m.p. 89°C), 8 (0.51 g, m.p. 237°C) and 6 (1.02 g, m.p. 135°C) consecutively.

6 : ν_{max} 3 400, 3 272, 2 928 and 1 304 cm^{-1}; EI m/z 192 (M^+), 174, 109, 96, 80; Calc. for $C_{12}H_{16}O_2$: C, 75.00; H, 8.33%. Found: C, 74.97; H, 8.31%.

7 : ν_{max} 3 224, 2 952 and 1 308 cm^{-1}; EI m/z 176 (M^+), 158, 143, 133, 117, 107, 95; Calc. for $C_{12}H_{16}O$: C, 81.82; H, 9.09%. Found: C, 81.78; H, 9.11%.

8 : ν_{max} 2 936, 2 864, 1 748, 1 444, 1 392, 1 156 and 1 080 cm^{-1}; EI m/z 190 (M^+), 162 (M^+-CO), 148, 80; Calc. for $C_{12}H_{14}O_2$: C, 75.79; H, 7.37%. Found: C, 75.76; H, 7.32%.

9 : ν_{max} 3 432, 2 936 and 1 132 cm^{-1}; EI m/z 192 (M^+), 147, 132, 91, 79; Calc. for $C_{12}H_{16}O_2$: C, 75.00; H, 8.33%. Found: C, 74.96; H, 8.30%.

Zinc-Hydrochloric Acid Reduction of 4

A mixture of 4 (0.6 g), zinc powder (2 g), concentrated hydrochloric acid (5 cm^3), water (10 cm^3) and methanol (10 cm^3) was boiled under reflux for 1 h and the products [6 (0.24 g), 8 (0.12 g) and 9 (0.08 g)] isolated as described before.

Clemmensen Reduction of 8

A mixture of 8 (0.6 g), zinc amalgam (5 g), concentrated hydrochloric acid (5 cm^3), water (5 cm^3) and methanol (10 cm^3) was boiled under reflux and the products [6 (0.34 g) and 9 (0.14 g)] isolated as described before.

Acetylation of 6

A mixture of 6 (0.2 g), sodium acetate (0.2 g) and acetic anhydride (20 cm^3) was boiled under reflux for 3 h. The reaction mixture was cooled and excess acetic anhydride hydrolised with water. The product (0.22 g, m.p. 63°C) was extracted with dichloromethane and recrystallised from ethanol. ν_{max} 2 928, 1 740, 1 368, 1 242 and 1 206 cm^{-1}; EI m/z 276 (M^+), 234 (M^+-CH_2CO), 192 (M^+-$2CH_2CO$). Calc. for $C_{16}H_{20}O_4$: C, 69.56; H, 7.25%. Found: C, 69.52; H, 7.23%.

Oxidation of 6 with Sodium Periodate

A mixture of 6 (0.2 g), aqueous sodium periodate (5%, 10 cm^3) and methanol (1 cm^3) was stirred at room temperature for 2 h. Dilution with water and extraction with dichloromethane produced 8 (0.14 g).

Reaction of 8 with Magnesium and Magnesium Iodide

A mixture of magnesium powder (1,5 g), diethyl ether (10 cm^3), benzene (15 cm^3), iodine (4.2 g) and 8 (1 g) was stirred at room temperature for 4 h. Dilution with water and extraction with benzene yielded 6 (0.8 g).

Bromination of 8

A solution of 8 (0.19 g) in acetic acid (5 cm^3) was refluxed with bromine (0.32 g) for 2 h. Dilution with water and extraction with dichloromethane yielded 14 (0.32 g, m.p. 196-200°C). ν_{max} 2 910, 1 750, 1 240, 1 124, 1 048 and 852 cm^{-1}; EI m/z 346 (M^+). Calc. for $C_{12}H_{12}Br_2O_2$: C, 41.42; H, 3.48%. Found: C, 41.46; H, 3.47%.

Pyrolysis of 14 with Copper Powder

14 (0.2 g) was heated (200°C) with copper powder (1 g) in a micro-oven for 0.5 h. The product 4 (0.05 g) sublimed as a colourless solid.

Reductive Dehalogenation of 14

A mixture of 14 (0.1 g), ethanol (5 cm^3) and activated zinc powder (0.2 g) was refluxed for 2 h. Dilution with water and extraction with diethyl ether yielded 8 (0.05 g).

Acetylation of 7

A mixture of 7 (0.3 g), sodium acetate (0.1 g) and acetic anhydride (20 cm^3) was boiled under reflux for 2 h. The cooled reaction mixture was stirred with a mixture of ethanol (10 cm^3) and water (10 cm^3). The colourless product (0.27 g, m.p. 54°C) was filtered off and recrystallised from ethanol. ν_{max} 2 920, 1 740, 1 365 and 1 235 cm^{-1}; EI m/z 218 (M$^+$), 176 (M$^+$-42). Calc. for $C_{14}H_{18}O_2$: C, 77.06; H, 8.26%. Found: C, 77.11; H, 8.28%.

Huang-Minlon Reduction of 4

A mixture of 4 (1 g), diethylene glycol (50 cm^3), 98% hydrazine hydrate (15 cm^3) and potassium hydroxide (8 g) was boiled under reflux for 1 h. The cooled reaction mixture was diluted with water, neutralised with diluted hydrochloric acid and extracted with diethyl ether. Removal of the excess ether under reduced pressure produced the colourless product 16 (0,4 g, m.p. 136°C). ν_{max} 2 943 cm^{-1}; EI m/z 160 (M$^+$), 131, 117, 104, 91, 80; Calc. for $C_{12}H_{16}$: C, 90.0; H, 10.0%. Found: C, 89.94; H, 9.96%.

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