PHOTOLYSIS OF HOMOCONJUGATED ALLENE KETONES[a]

Walentina Kudrawcew, Bruno Frei, Hans Richard Wolf[b], and Oskar Jeger*
Laboratorium für Organische Chemie der Eidgenössischen Technischen Hochschule, Universitätstrasse 16, 8092 Zürich, Switzerland

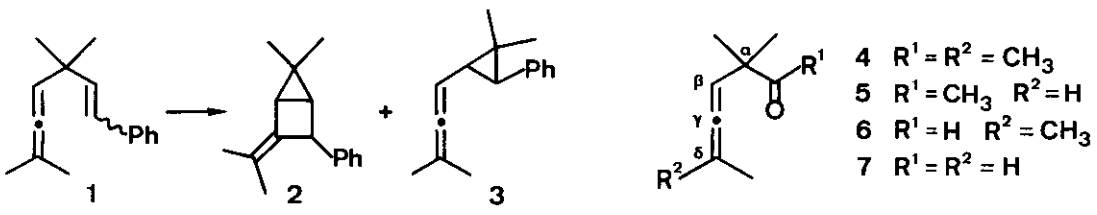
Dedicated to Prof. Dr. Kyosuke Tsuda on the occasion of his 75th birthday

Abstract - UV-Irradiation (λ>280 nm) of the homoconjugated allene ketones 4 and 5 gives, in addition to small amounts of the ketodienes 8 and 17 (1,3-acyl shift), the enol ethers 9, 10 and 18, 19 respectively (cyclization process followed by 1,5-H-shift). However, on T-sensitization in acetone, 4 forms the spirodioxetane 13 in high yield. Irradiation of 4 in 2-propanol or ethanol affords the acetals 11 and 12.

INTRODUCTION

The photochemistry of a di-π-methane system containing an allene moiety was investigated some years ago by Griffin et al.[2] Thus, on UV-irradiation (λ=254 nm) compound 1 was isomerized to the "housane" 2 as the main product ([2+2]-cycloaddition) and to a smaller extent to the cyclopropylallene 3 (di-π-methane rearrangement).

Scheme 1



[a] Photochemical Reactions, 124th communication.[1]

[b] F. Hoffmann - La Roche & Co. Ltd., CH-4002 Basle, Switzerland.

In the present investigation the photochemistry of the homoconjugated allene ketones 4 and 5 (Scheme 1) is studied. These ketones have geminal dialkyl substituent in the α-position to the keto function. Therefore it seemed necessary to check whether α-cleavage (Norrish Type I) would be the main photoprocess and how the γ,δ-double bond of the allene moiety would participate in isomerizations such as a 1,3-acyl shift and/or an oxa-di-π-methane rearrangement.[3,4] The allene ketones 4 (94% yield) and 5 (91% yield) were obtained from the reaction of the aldehydes 6 and 7[5] respectively (Scheme 1) with methylmagnesium iodide followed by Jones oxidation.

RESULTS

The irradiation products (λ>280 nm) are shown in Scheme 2, and the product distribution is given in Tables 1 and 2.

Scheme 2

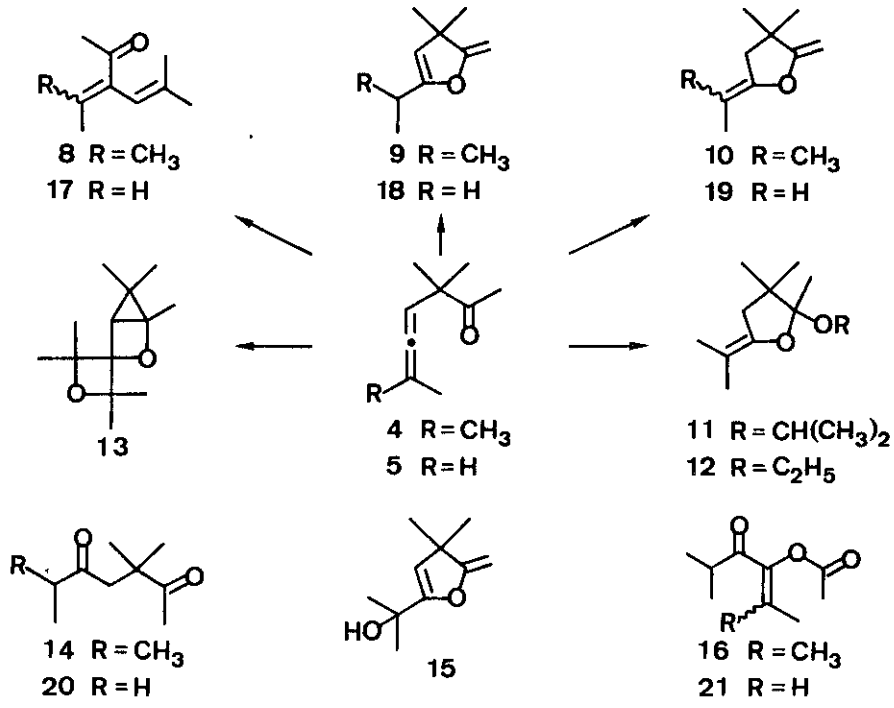


Table 1: Results of the photolysis of 4

solvent	conversion [%]	product distribution [%][e]								
		8	9	10	11	12	13	14[6]	15	16
pentane	80[c]	7	2	17	--	--	3	16	--	--
pentane	57[d]	1	~1	5	--	--	3	15	16	3
cyclohexane	85[c]	3	3	30	--	--	2	2	--	--
cyclohexane	64[d]	6	--	19	--	--	5	5	22	5
acetone	70[c]	3	5	~1	--	--	45	6	--	--
acetone	85[d]	10	2	--	--	--	70	--	6	--
ethanol	93[c]	~1	~1	8	--	48	--	1	--	2
ethanol	90[d]	3	~1	8	--	40	--	--	--	1
2-propanol	90[c]	~1	5	12	31	--	--	2	--	2
2-propanol	80[d]	6	--	2	48	--	--	24	--	3
1,1,2-trichloro-trifluoroethane	85[c]	2	12	17	--	--	--	13	4	4
	80[d]	4	16	20	--	--	--	12	10	17

Table 2: Results of the photolysis of 5 in pentane

conversion [%]	product distribution [%][e]				
	17[f]	18	19	20	21
50[c]	<1	35	1	8	4
60[d]	<1	26	5	4	-

[c] Analytical scale: the product distribution was determined by capillary GC-analysis (UCON 50 HB-5100; temperature program, 35-150°) of the photolysis solution using hexadecane as an internal standard.

[d] Preparative scale: the relative product distribution was estimated by the weight of the distillate of the reaction mixture in combination with GC-analysis (Carbowax 20M, 150° and 5% SE-30, 130° for the photolysis mixtures from 4 and 5 respectively).

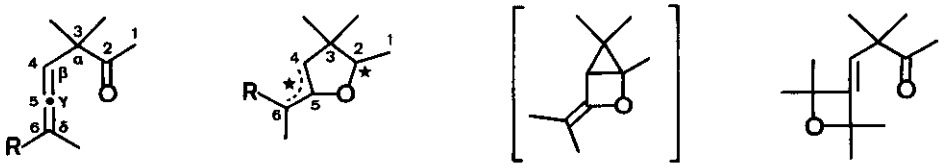
[e] Based on converted starting material.

[f] Identified by IR only, comparison with the IR-spectrum of 8.

DISCUSSION

The allene ketones 4 and 5 undergo (to a small extent) α-cleavage followed by a 1,3-acyl shift (4 • 8, 5 → 17), thus showing the typical behaviour of β,γ-unsaturated ketones.[4] However, the photoisomerizations 4 → 9 and 10, and 5 → 18 and 19 are predominant. These conversions presumably include the intermediate a which could undergo 1,5-H-shifts from C(1) to C(4) or C(6) (Scheme 3).[g] In 2-propanol or ethanol, intermediate a has been trapped by solvent addition yielding 11 and 12 respectively.

Scheme 3



Regarding the light induced (λ>280 nm) formation of the spirodioxetane 13 in pentane and cyclohexane, a mechanistic discussion seems to be premature.[g] However, on photolysis of 4 in acetone, 13 is obviously formed by solvent addition (see also photolysis of 4 in acetone-d_6, footnote p and exper. part). It can be hypothesized that acetone is added to the bicyclic intermediate 22 arising from bond formation between C(2) and C(4) in a (Scheme 3). However, it should also be considered that initial intermolecular cycloaddition of acetone to the allene system (4 → 24)[h,i] is followed by intramolecular Paterno-Büchi addition of the

---

[g] Experiments to disclose the mechanisms are in progress.

[h] Compound 24 was obtained by hydrogenolysis of 13 (cf. infra).

[i] For a discussion of cycloadditions of carbonyl compounds to allenes, see Hammond.[7]

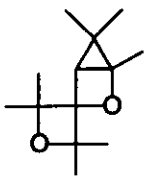
carbonyl group to the β,γ double bond (24 → 13).[k,l]

The aliphatic diketones 14 and 20 (Scheme 2) are formed by hydrolysis of 9 or 10 and 18 or 19 respectively. The tertiary alcohol 15 and the compounds 16 and 21 are oxidation products presumably arising during work up of the photolysis. In conclusion, it is remarkable that from irradiation of the homoconjugated allene ketones 4 and 5 no products resulting from an oxa-di-π-methane rearrangement were detected. Also astonishing is that the 1,3-acyl shift (4 → 8, 5 → 17) seems to be a minor process. It has been shown that in non polar solvents the main reaction is isomerization to cyclic enol ethers (4 • 9, 10; 5 → 18, 19), whereas in acetone solution, oxetane formation and addition of solvent (4 • 13) is predominant.

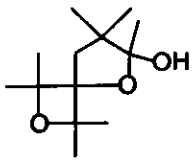
TRANSFORMATIONS OF THE PHOTOPRODUCTS

The spirodioxetane 13 was hydrolyzed (20% H_2SO_4) to the hemiacetal 29 (85%; Scheme 5). Reductive ether cleavage of 13 ($LiAlH_4$, N-methylmorpholine) according

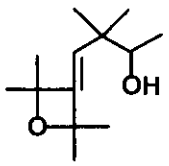
Scheme 5



13



29

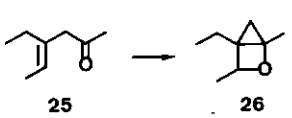


30

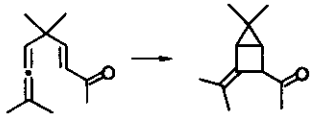
---

k An intramolecular oxetane formation of this type has been reported by Engel[8] (25 → 26).

Scheme 4



25 26



27 28

l On n,π*-irradiation the related enone 27 undergoes [2+2]-cycloaddition furnishing the "housane" compound 28 in ~70% yield.[9]

to the method of Sauers[10] gave the alcohol 30 (77%) which was also obtained from hydrogenolysis (Lindlar catalyst) of 13 to give 24 (55%; Scheme 3) followed by $NaBH_4$-reduction of the latter.

Hydrolysis (oxalic acid, methanol) of the enol ethers 9, 10 and 18, 19 afforded the diketones 14 and 20 respectively in quantitative yield (Scheme 2).

ANALYTICAL DATA[m]

3,3,6-Trimethyl-4,5-heptadien-2-one (4):[n] bp 80°/10 mm; UV: 298 (193); IR: 1965, 1708; ^{1}H-NMR: 1.1 (s, $2H_3C$-C(3)), 1.69 (d, J=3, H_3C-C(6), 3H-C(7)), 2.02 (s, 3H-C(1)), 4.92 (septet, J=3, H-C(4)); ^{13}C-NMR: 20.3, 24.4, 24.9 (5qa, 2qa superimposed at 20.3 and 24.4), 95.6 (d, C(4)), 48.6 (s, C(3)), 98.4 (s, C(6)), 201.3 (s, C(5)), 210.9 (s, C(2)); MS: 152 (<1, M^+), 137 (100).

3,3-Dimethyl-4,5-heptadien-2-one (5):[n] bp 30°/0.05 mm; UV: 298 (180); IR: 1920, 1715; ^{1}H-NMR(300 MHz, $CDCl_3$): 1.21, 1.22 (2s, $2H_3C$-C(3)), 1.69 (dxd, J_1=6, J_2=3, 3H-C(7)), 2.16 (s, 3H-C(1)), 5.15 (dxqa, J_1=6, J_2=3, H-C(4)), 5.27 (dxqa, J_1=J_2=6, H-C(6)); ^{13}C-NMR: 14.2, 24.3, 25.0 (4qa, 2qa superimposed at 24.3), 88.7, 96.9 (2d, C(4), C(6)), 48.2 (s, C(3)), 204.2 (s, C(5)), 210.6 (s, C(2)); MS: 138 (<1, M^+), 123 (100).

5-Methyl-3-isopropylidene-4-hexen-2-one (8): bp 40°/0.05 mm; UV: 210 (14500), 235S (12600); IR: 1688, 1682, 1600; ^{1}H-NMR($CDCl_3$, ~90% pure): 1.50 (m, $w_{1/2}$=4) and 1.68 (s, $(H_3C)_2C$=C(3)), 1.79, 1.90 (2d, J=2, H_3C-C(5), 3H-C(6), 2.10 (s, 3H-C(1)), 5.80 (m, $w_{1/2}$=8, H-C(4)); ^{13}C-NMR: 19.2, 21.8, 22.7, 25.4, 30.3 (5qa), 121.6 (d, C(4)), 135.2, 137.4, 141.7 (3s, C(3), C(5), $(H_3C)_2$C=C(3)), 203.6 (s, C(2)); MS: 152 (71, M^+), 137 (96), 67 (100).

3,3-Dimethyl-2-methylidene-5-isopropyl-2,3-dihydrofurane (9):[o] UV: 229 (12900); IR: 1685, 1655, 1625, 1230, 1170, 1150, 1116, 1060, 1045, 955; ^{1}H-NMR($CDCl_3$): 1.09 (d, J=6, $(H_3C)_2$CH-C(5)), 1.15 (s, $2H_3C$-C(3)), 2.40 (dxseptet, J_1=6, J_2=1,

---

[m] IR and ^{1}H-NMR(100 MHz) spectra were recorded in CCl_4, ^{13}C-NMR(25.2 MHz) spectra in $CDCl_3$ and UV spectra in pentane.

[n] Correct C,H microanalysis values were obtained.

[o] Isolated by preparative GC.

$(H_3C)_2CH$-C(5)), 3.98 (d, J=2) and 4.38 (m, $w_{1/2}$=4.5, H_2C=C(2)), 4.66 (m, $w_{1/2}$=4, H-C(4)); MS: 152 (18, M^+), 137 (100).

3,3-Dimethyl-2-methylidene-5-isopropylidenetetrahydrofurane (10):[n,o] UV: 215 (8400); IR: 1665, 1625, 1205, 1175, 1130, 980; ^{1}H-NMR(C_6D_6): 1.00 (s, $2H_3C$-C(3)), 1.45 (m, $w_{1/2}$=3) and 1.76 (m, $w_{1/2}$=4, $(H_3C)_2$C=C(5)), 2.02-2.16 (m, 2H-C(4)), 4.82, 5.42 (2d, J=2, H_2C=C(2)); ^{13}C-NMR: 16.6, 18.7, 27.7 (4qa, 2qa superimposed at 27.7), 40.9 (t, C(4)), 78.8 (t, H_2C=C(2)); 40.1 (s, C(3)), 100.7 (s, $(CH_3)_2$C=C(5)), 145.9, 170.6 (2s, C(2), C(5)); MS: 152 (100, M^+), 137 (73), 109 (12).

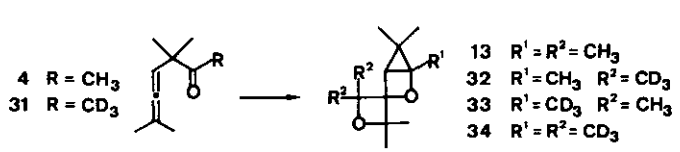
2,3,3-Trimethyl-2-isopropoxy-5-isopropylidenetetrahydrofurane (11):[n,o] IR: 1715, 1185, 1170, 1150, 1130, 1075; ^{1}H-NMR($CDCl_3$): 0.89, 1.05 (2s, $2H_3C$-C(3)), 0.97, 1.04 (2d, J=6, $(H_3C)_2$CH-O), 1.24 (s, H_3C-C(2)), 1.50 (m, $w_{1/2}$=3) and 1.60 (m, $w_{1/2}$=6, $(H_3C)_2$C=C(5)), 2.29 (AB-system, J=14, δ_A=2.12, δ_B=2.46, 2H-C(4)), 4.00 (septet, J=6, $(H_3C)_2$CH-O); ^{13}C-NMR: 16.3, 16.4, 18.8, 21.3, 23.9, 24.4, 25.3 (7qa), 40.9 (t, C(4)), 63.5 (d, $(H_3C)_2$CH-O), 44.2 (s, C(3)), 98.4 (s, C(2)), 109.7 (s, $(H_3C)_2$C=C(5)), 146.9 (s, C(5)); MS: 212 (26, M^+), 170 (28), 153 (51), 86 (100).

2-Ethoxy-2,3,3-trimethyl-5-isopropylidenetetrahydrofurane (12):[o] IR: 1715, 1180, 1150, 1110, 1080, 1045; ^{1}H-NMR($CDCl_3$): 0.90, 1.20 (2s, $2H_3C$-C(3)), 1.06 (t, J=6, H_3CCH_2-O), 1.24 (s, H_3C-C(2)), 1.50 (m, $w_{1/2}$=3) and 1.60 (m, $w_{1/2}$=5, $(H_3C)_2$C=C(5)), 2.29 (AB-system, J=14, δ_A=2.10, δ_B=2.49, 2H-C(4)), 3.47 (m with qa character, J=6, H_3CCH_2-O); ^{13}C-NMR: 15.3, 15.8, 16.3, 18.8, 21.3, 25.4 (6qa), 40.8 (t, C(4)), 56.4 (t, H_3CCH_2-O), 44.2 (s, C(3)), 98.8 (s, C(2)), 109.3 (s, $(H_3C)_2$C=C(5)), 146.6 (s, C(5)); MS: 198 (60, M^+), 153 (74), 137 (34), 127 (17), 95 (100).

1,5,5,2',2',4',4'-Heptamethyl-2-oxabicyclo[2.1.0]pentane-3-spiro-3'-oxetane (13):[n] bp 50°/0.03 mm; IR: 1180, 1140, 1115, 1080, 1035, 935, 925, 910; ^{1}H-NMR:[p]

[p] The assignment of the methyl signals is based on comparison of the spectrum of 13 with those of the corresponding deuterated compounds 32-34 obtained from irradiation of 4 and 31 in acetone and acetone-d_6.

Scheme 6



0.90 (s, H_3C-C(5)), 1.18 (s, H_3C-C(5), $2H_3C$-C(4')), 1.27, 1.30 (2s, $2H_3C$-C(2')), 1.40 (s, H-C(4)), 1.46 (s, H_3C-C(1)); ^{13}C-NMR: 12.8, 15.5, 20.8, 24.4, 24.9, 26.6, 27.3 (7qa), 25.2 (d, C(4)), 27.0 (s, C(5)), 71.4, 84.0, 84.5, 86.7 (4s, C(1), C(3), C(2'), C(4')); MS: 210 (<1, M^+), 167 (18), 153 (16), 152 (12), 137 (86), 43 (100).

3,3-Dimethyl-2-methylidene-5-(2'-hydroxyprop-2'-yl)-2,3-dihydrofurane (15):° IR: 3600, 3480, 1690, 1660, 1630; ^{1}H-NMR: 1.16 (s, $2H_3C$-C(3)), 1.32 (s, $(H_3C)_2$C(2')), 1.70 (s, HO), 3.94 (d, J=2) and 4.34 (dxd, $J_1=J_2=2$, H_2C=C(2)), 4.80 (m, $w_{1/2}=3$, H-C(4)). ^{13}C-NMR: 27.6 (2qa) and 29.7 (2qa), 81.1 (t, H_2C=C(2)), 106.2 (d, C(4)), 45.3 (s, C(3)), 68.3 (s, C(2')), 158.9, 172.3, (2s, C(2), C(5)); MS: 168 (35, M^+), 153 (66), 138 (18), 43 (100).

2,5-Dimethyl-4-oxo-2-hexen-3-yl acetate (16):^{n} bp 50°/0.05 mm; UV: 235 (8700); IR: 1755, 1695, 1625, 1210; ^{1}H-NMR(~90% pure): 0.99 (d, J=7, H_3C-C(5), 3H-C(6)), 1.69, 2.08 (2s, H_3C-C(2), 3H-C(1)), 2.13 (s, H_3CCO_2-), 2.64 (septet, J=7, H-C(5)); ^{13}C-NMR: 18.2, 20.0, 20.5, 23.7 (5qa, 2qa superimposed at 18.2), 36.4 (d, C(5)), 137.6, 140.2 (2s, $(H_3C)_2$C=C(3)), 169.5 (s, H_3CCO_2-), 201.0 (s, C(4)); MS: 184 (6, M^+), 142 (52), 43 (100).

5-Ethyl-3,3-dimethyl-2-methylidene-2,3-dihydrofurane (18):° IR: 1685, 1655, 1625, 1230, 1195, 1150, 1120, 1055, 1000, 980; ^{1}H-NMR(300 MHz, C_6D_6): 1.10 (t, J=7.5, H_3CCH_2-C(5)), 1.20 (s, $2H_3C$-C(3)), 2.19 (qaxd, $J_1=7.5$, $J_2=1.5$, H_3C-CH_2-C(5)), 4.00 (dxd, $J_1=2.5$, $J_2=0.5$) and 4.41 (dxd, $J_1=2.5$, $J_2=1.5$, H_2C=C(2)), 4.72 (d, J=1.5, $w_{1/2}=3$, H-C(4)); MS: 138 (19, M^+), 123 (100).

5-Ethylidene-3,3-dimethyl-2-methylidenetetrahydrofurane (19):° IR: 1670, 1625, 1200, 1180, 1130, 1090, 1070, 1010; ^{1}H-NMR(300 MHz, C_6D_6, ~90% pure): 0.97 (s, $2H_3C$-C(3)), 1.77 (dxt, $J_1=7$, $J_2=2$, H_3CCH=C(5)), 2.05 (m, $w_{1/2}=3$, 2H-C(4)), 3.88, 4.52 (2d, J=2, H_2C=C(2)), 4.28 (qaxt, $J_1=7$, $J_2=1.8$, H_3CCH=C(5)), MS: 138 (100, M^+), 123 (73), 95 (19).

3,3-Dimethyl-2,5-heptanedione (20): bp 55°/0.05 mm; IR: 1715, 1705; ^{1}H-NMR: 0.98 (t, J=7, 3H-C(7)), 1.12 (s, $2H_3C$-C(3)), 2.08 (s, 3H-C(1)), 2.29 (qa, J=7, 2H-C(6)), 2.55 (s, 2H-C(4)); MS: 156 (8, M^+), 127 (26), 57 (100).

5-Methyl-4-oxo-2-hexen-3-yl acetate (21): bp 50°/0.05 mm; IR: 1765, 1690, 1660, 1645, 1225, 1200; ^{1}H-NMR: 1.06 (d, J=7, H_3C-C(5), 3H-C(6)), 1.74 (d, J=7, 3H-C(1)), 2.15 (s, H_3CCO_2-), 2.97 (septet, J=7, H-C(5)), 6.36 (qa, J=7, H-C(2));

MS: 170 (<1, M^{+}), 128 (29), 127 (27), 43 (100).

2,2-Dimethyl-1-(2',2',4',4'-tetramethyl-1'-oxacyclo-3'-butylidene)-3-butanone (24): ^{n} bp 55°/0.05 mm; UV: 295 (160); IR: 1705, 1210, 1175, 1115, 1105, 915; ^{1}H-NMR(90 MHz): 1.20, 1.35, 1.45 (6s, two by two superimposed, $6H_3C$), 2.08 (s, 3H-C(4)), 5.3 (s, H-C(1)); ^{13}C-NMR: 25.6, 29.0, 29.3 (7qa, 3qa superimposed at 25.6, two by two superimposed at 29.0 and 29.3), 122.8 (d, C(1)), 48.6 (s, C(2)), 83.2, 86.0 (2s, C(2'), C(4')), 153.5 (s, C(3')), 210.3 (s, C(3)); MS: 210 (<1, M^{+}), 195 (<1), 153 (32), 152 (24), 137 (38), 43 (100).

1,1,3,3,6,7,7-Heptamethyl-2,5-dioxaspiro[3.4]octan-6-ol (29): bp 80°/0.03 mm; IR: 3595, 3490, 1180, 1165, 1155, 1135, 1115, 1100, 950; ^{1}H-NMR($CDCl_3$): 0.95, 1.10, 1.26, 1.30, 1.33, 1.42 (7s, 2s superimposed at 1.26, $7H_3C$), 1.78 (AB-system, J=13, δ_A=2.62, δ_B=2.89, 2H-C(8)), 2.03 (s, HO); ^{13}C-NMR: 14.7, 22.2, 24.5, 25.9, 27.6, 28.0, 29.4 (7qa), 40.6 (t, C(8)), 46.2 (s, C(7)), 71.5, 83.4, 93.0, 109.9 (4s, C(1), C(3), C(4), C(6)); MS: 228 (<1, M^{+}), 170 (34), 155 (14), 154 (29), 43 (100).

2,2-Dimethyl-1-(2',2',4',4'-tetramethyl-1'-oxacyclo-3'-butylidene)-3-butanol (30): bp 60°/0.03 mm; IR: 3625, 3570, 3450, 1210, 1180, 1105, 1080, 910; ^{1}H-NMR ($CDCl_3$): 1.03 (s, $2H_3C$-C(2)), 1.11 (d, J=7, 3H-C(4)), 1.37 (2s) and 1.55 (2s, $2H_3C$-C(2'), $2H_3C$-C(4')), 1.71 (br.s, HO), 3.49 (qa, J=7, H-C(3)), 4.94 (s, H-C(1)); ^{13}C-NMR: 18.2, 23.9, 24.4, 29.4, 30.3 (7qa, 2qa superimposed at 29.4 and 30.3), 74,7 (d, C(3)), 124.9 (d, C(1)), 40.5 (s, C(2)), 83.9, 86.5 (2s, C(2'), C(4')), 150.9 (s, C(3')); MS: 197 (2, M^{+}-15), 167 (12), 153 (48), 43 (100).

Acknowledgement - This work was carried out with the financial support of the Swiss National Science Foundation and Ciba-Geigy Ltd., Basle.

EXPERIMENTAL

General. - See Ref. 11. Photolysis experiments were carried out under argon with a 125 W Hg medium pressure lamp (Philips) behind pyrex, on analytical scale in NMR-tubes and on preparative scale in an immersion well apparatus. Chromatographies ("flash") were performed on SiO_2 (Merck) according to Still et al.[12]

1. Preparation of 4 and 5. - 1.1. Allene ketone 4. - To a Grignard solution prepared from 3.4 g (0.14 mol) of Mg and 20 g (0.14 mol) of methyl iodide in 150 ml dry ether was added a solution of 15 g (0.11 mol) of 6[5] in 50 ml dry ether. After stirring for 2 hr, the mixture was treated with aq. NH_4Cl and worked up. Chromatography (ether/hexane 3:7) afforded 16.5 g of 3,3,6-trimethyl-4,5-heptadien-2-ol which was dissolved in 150 ml acetone, cooled to 10° and treated with an excess of Jones reagent. The mixture was worked up and chromatographed (ether/hexane 1:9) to give 15.7 g (94%) of 4. - 1.2. Allene ketone 5. - According to 1.1., reaction of a Grignard solution prepared from 4.6 g (0.19 mol) of Mg and of 27 g (0.19 mol) of methyl iodide in 70 ml dry ether with 21.5 g (0.17 mol) of 7[5] in 200 ml dry ether followed by Jones oxidation gave 21.7 g (91%) of 5.

2. Photolysis experiments. - 2.1. Irradiation of 4. - 2.1.1. In pentane. (a) A solution of 30 mg (0.20 mmol) of 4 and 15 mg (0.07 mmol) of hexadecane in 1 ml pentane was irradiated giving[c,e,q] 7% 8, 2% 9, 17% 10, 3% 13, 16% 14. (b) A solution of 5.0 g (33 mmol) of 4 in 480 ml pentane was irradiated giving[d,e,q] 1% 8, ~1% 9, 5% 10, 3% 13, 15% 14, 16% 15, 3% 16. - 2.1.2. In cyclohexane. (a) A solution of 30 mg (0.20 mmol) of 4 and 14 mg (0.06 mmol) of hexadecane in 1 ml cyclohexane was irradiated giving[c,e,q] 3% 8, 3% 9, 30% 10, 2% 13, 2% 14. (b) A solution of 2.5 g (16 mmol) of 4 in 220 ml cyclohexane was irradiated giving[d,e,q] 6% 8, 19% 10, 5% 13, 5% 14, 22% 15, 5% 16. - 2.1.3. In acetone. (a) A solution of 40 mg (0.26 mmol) of 4 and 18 mg (0.08 mmol) of hexadecane in 1.5 ml acetone was irradiated giving[c,e,q] 3% 8, 5% 9, ~1% 10, 45% 13, 6% 14. (b) A solution of 4.5 g (30 mmol) of 4 in 420 ml acetone was irradiated giving[d,e,q] 10% 8, 2% 9, 70% 13, 6% 15. - 2.1.4. In ethanol. (a) A solution of 30 mg (0.20 mmol) of 4 and 14 mg (0.06 mmol) of hexadecane in 1 ml ethanol was irradiated giving[c,e,q] ~1% 8, ~1% 9, 8% 10, 48% 12, 1% 14, 2% 16. (b) A solution of 1.0 g (6.6 mmol) in 100 ml ethanol was irradiated giving[d,e,q] 3% 8, ~1% 9, 8% 10, 40% 12, 1% 16. - 2.1.5. In 2-propanol. (a) A solution of 40 mg (0.26 mmol) of 4 and 20 mg (0.09 mmol) of hexadecane in 1.5 ml 2-propanol was irradiated giving[c,e,q] ~1% 8, 5% 9, 12% 10, 31% 11, 2% 14, 2% 16. (b) A solution

---

[q] The conversion is indicated in Table 1 or 2, respectively.

of 4.8 g (32 mmol) of 4 in 400 ml 2-propanol was irradiated giving[d,e,q] 6% 8, 2% 10, 48% 11, 24% 14, 3% 16. - 2.1.6. In 1,1,2-trichlorotrifluoroethane. (a) A solution of 30 mg (0.20 mmol) of 4 and 18 mg (0.08 mmol) of hexadecane in 1 ml 1,1,2-trichlorotrifluoroethane was irradiated giving[c,e,q] 2% 8, 12% 9, 17% 10, 13% 14, 4% 15, 4% 16. (b) A solution of 1.0 g (6.6 mmol) of 4 in 100 ml 1,1,2-trichlorotrifluoroethane was irradiated giving[d,e,q] 4% 8, 16% 9, 20% 10, 12% 14, 10% 15, 17% 16. - 2.2. Irradiation of 5 in pentane. (a) A solution of 30 mg (0.22 mmol) of 5 and 14 mg (0.06 mmol) of hexadecane was irradiated giving[c,e,q] <1% 17, 35% 18, 1% 19, 8% 20, 4% 21. (b) A solution of 6 g (43 mmol) of 5 in 500 ml pentane was irradiated giving[d,e,q] <1% 17, 26% 18, 5% 19, 4% 20.

3. Transformations of the photoproducts. - 3.1. Spirodioxetane 13. - 3.1.1. Hydrolysis of 13. A solution of 45 mg (0.21 mmol) of 13 in 4 ml H_2SO_4(20%) was stirred for 24 hr at RT. The mixture was worked up and chromatographed using hexane/ether 1:1 to yield 41 mg (85%) of 29. - 3.1.2. Reductive ether cleavage of 13. To 270 mg (7.1 mmol) of $LiAlH_4$ in 10 ml N-methylmorpholine was added a solution of 80 mg (0.38 mmol) of 13 in 20 ml N-methylmorpholine. The mixture was heated under reflux for 65 hr, cooled to 0°, acidified with aq HCl (2%) and extracted with CH_2Cl_2. Chromatography (ether/hexane 3:2) gave 62 mg (77%) of 30. - 3.1.3. Hydrogenolysis of 13. A solution of 100 mg (0.48 mmol) of 13 in 15 ml pentane and 45 mg of Lindlar catalyst was stirred for 50 hr under H_2. The mixture was filtered through Celite. Chromatography (ether/hexane 1:1) afforded 55 mg (55%) of 24. - 3.1.4. $NaBH_4$-reduction of 24. To a solution of 35 mg (0.17 mmol) of 24 in 15 ml methanol was added a solution of 20 mg (0.53 mmol) of $NaBH_4$ in 2 ml of 1:1 methanol/H_2O. The mixture was stirred for 2 hr and worked up giving 34 mg (93%) of 30. - 3.2. Hydrolysis of 9, 10, 18 and 19. (a) To the solutions of 5 mg (0.03 mmol) of 9 and 10, respectively, in 5 ml of methanol was added 1 mg (0.01 mmol) of oxalic acid. Work up of the mixtures gave quantitatively 14.[5] (b) To the solutions of 5 mg (0.04 mmol) of 18 and 19, respectively, in 5 ml of methanol was added 1 mg (0.01 mmol) of oxalic acid. Work up of the mixtures afforded 20 in quantitative yield.

We are indebted to the following persons for their help: Miss B. Brandenberg and Mr. K. Hiltbrunner (NMR); Mrs. L. Golgowski and Prof. J. Seibl (MS) and

Mr. D. Manser (elemental analysis). We are also grateful to Mr. K. Job for the preparation of starting materials and to Dr. T. Lyle for his help in compilation of the English manuscript.

REFERENCES

1. 123rd communication: S. Iwasaki, Heterocycles, this issue.
2. D.C. Lankin, D.M. Chihal, G.W. Griffin and N.S. Bhacca, Tetrahedron Lett., 1973, 4009.
3. W.G. Dauben, G. Lodder and J. Ipaktschi, Top. Current Chem., 1975, 54, 73.
4. K.N. Houk, Chem. Rev. 1976, 76, 1.
5. R.S. Bly and S.U. Koock, J. Amer. Chem. Soc., 1969, 91, 3292.
6. C. Chassin, E.A. Schmidt and H.M.R. Hoffmann, J. Amer. Chem. Soc., 1974, 96, 606.
7. H. Gotthardt, R. Steinmetz and G.S. Hammond, J. Org. Chem., 1968, 33, 2774.
8. P.S. Engel and M.A. Schexnayder, J. Amer. Chem. Soc., 1972, 94, 4357.
9. Unpublished results by B. Frei.
10. R.R. Sauers and J.A. Whittle, J. Org. Chem., 1969, 34, 3579.
11. A.P. Alder, H.R. Wolf and O. Jeger, Helv. Chim. Acta, 1980, 63, 1833.
12. W.C. Still, M. Kahn and A. Mitra, J. Org. Chem., 1978, 43, 2923.

Received, 1st August, 1981