1465, 1358, 1300, 1197, 1057, 1019, 848, 714. ^{1}H-NMR.: 1.52/*m* ($W^{1/2}$ approx. 8), H_2–C(2) and –C(7); 2.38/*m* ($W^{1/2}$ approx. 8), H–C(1), –C(3), –C(6) and –C(8); 6.20/*m* ($W^{1/2}$ approx. 8), H–C(4), –C(5), –C(9) and –C(10); the signals at 1.52 and 6.20 are changed to singlets in double irradiation experiments (simultaneous irradiation of the H–C(1), –C(3), –C(6) and –C(8) nuclei). ^{13}C–NMR.: only three signals due to the high symmetry (point group D_2) at 28.61/*d*, C(1), C(3), C(6) and C(8); 49.10/*t*, C(2) and C(7); 134.94/*d*, C(4), C(5), C(9) and C(10)].

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8. Synthesis of Bromo-substituted 2-Buten- and 2-Penten-4-olides

by **Christopher B. Chapleo**[1], **Karen L. Svanholt**[2], **Roger Martin** and **André S. Dreiding**

Organisch-Chemisches Institut der Universität Zürich, Rämistrasse 76, 8001 Zürich

(4. XI. 75)

Zusammenfassung. Durch Erhitzen mit Bromwasserstoffsäure lassen sich aus Methyl (2*Z*)-4-Brom-2-brommethyl-2-butenoat (**1**) bzw. -2-pentenoat (**3**) die Lactone 2-Brommethyl-2-buten-4-olid (**2**) bzw. -2-penten-4-olid (**4**) gewinnen. Unter den gleichen Bedingungen werden Methyl (2*Z*)- und (2*E*)-4,4-Dibrom-2-brommethyl-2-butenoat (**5** und **6**) nur zu den entsprechenden Säuren **7** und **8** hydrolysiert. Die (2*Z*)- resp. (2*E*)-Konfiguration von **7** und **8** werden durch die folgenden (*trans*/*cis* > 1) ^{13}C zu ^{1}H Kopplungen zwischen den an der Doppelbindung vicinal gelegenen Kohlenstoff- und Wasserstoffatomen im ^{13}C-NMR.-Spektrum bestätigt: ^{13}COO zu H—C(3) 5,7 Hz in **7** und 10,2 Hz in **8**; $^{13}CH_2Br$ zu H—C(3) 8,7 Hz in **7** und 6,9 Hz in **8**.

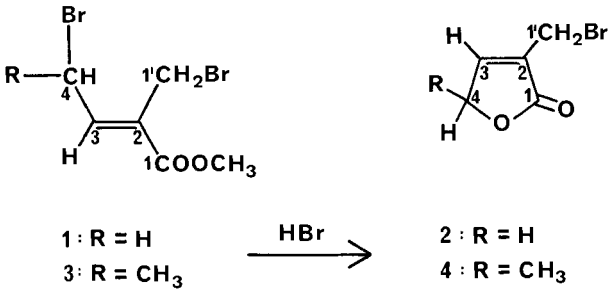
Mittels N-Bromsuccinimid werden 2-Buten-4-olid (**10**) bzw. sein 2-Methylderivat **12** in 4-Brom-2-buten-4-olid (**11**) bzw. sein 2-Methylderivat **13** übergeführt. Mit Methanol entsteht aus **13** 4-Methoxy-2-methyl-2-buten-4-olid (**14**). Die Bromierung von 2-Penten-4-olid (**15**) oder von 3-Penten-4-olid (**16**) unter denselben Bedingungen gibt hingegen 4,5-Dibrom-2-penten-4-olid (**17**), während aus 2-Brommethyl-2-penten-4-olid (**4**) ein Gemisch von 4-Brom-2-brommethyl-2-penten-4-olid (**20**) und 4,5-Dibrom-2-brommethyl-2-penten-4-olid (**21**) entsteht.

1. Introduction. – Brominated butenolides might be useful synthons for natural products containing an unsaturated butyrolactone moiety[3]. We describe here our

[1] Post-doctoral fellow 1972–1975.
[2] Present address: Maglemosevej 43, 2900 Hellerup, Danmark.
[3] Recent attention has been directed towards the synthesis of α-methylidene-butyrolactone derivatives [1], strigol [2] and related compounds [3] as well as freelingyne [4].

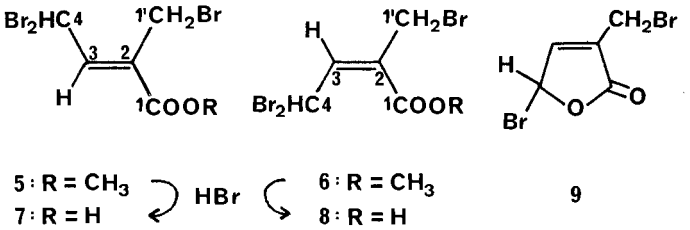
experience in preparing such compounds from intermediates available to us, namely from dibrominated unsaturated esters [5] [6] and from simple butenolides [7].

2. Acid hydrolysis of unsaturated dibromo-esters. – Heating methyl (2*Z*)-4-bromo-2-bromomethyl-2-butenoate (**1**) and methyl (2*Z*)-4-bromo-2-bromomethyl-2-pentenoate (**3**) [5] [6] with 48% aqueous hydrobromic acid gave 55% and 37% of



2-bromomethyl-2-buten-4-olide (**2**) and 2-bromomethyl-2-penten-4-olide (**4**), respectively. The structures of lactones **2** and **4** are evident from the physical properties given in the Exper. Part and listed partially in the Table. If **1** and **3** have indeed the (2*Z*)-configuration as postulated [6], the hydrolysis of the ester group must have been in both cases accompanied by isomerization at the double bond permitting the lactonization (compare [8]).

No such lactonization was observed with the two isomeric tribromo-esters methyl (2*Z*)- and (2*E*)-4,4-dibromo-2-bromomethyl-2-butenoates (**5** and **6**): When a sample

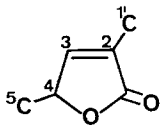


consisting of 40% of **5** and **6** (ratio 4:1), along with 60% of **1**, was subjected to the aqueous HBr treatment, a mixture of the two tribromo-acids **7** and **8** (ratio 4:1) was obtained, along with the bromo-lactone **2**, the latter arising from the dibromo-ester **1**. The dibromo-lactone **9** was not found.

The structures of **7** and **8** could be deduced in the mixture by the mass spectrum (M^+ = 340, 338, 336, 334 *m/e*) and the ^{1}H-NMR.-spectrum, which has signals for both isomers and is very similar to that described [6] for the mixture of the esters **5** and **6**.

It may be recalled that the assignment of the (*Z*)- and (*E*)-configurations [6] to the esters **5** and **6**, respectively, are based on the ^{1}H-NMR.-chemical shifts of H–C(4), the one in **6** (*cis* to $COOCH_3$) being at lower field ($\delta = 6.70$) than the one in **5** ($\delta = 6.42$). A similar difference in the ^{1}H-NMR.-chemical shifts for H–C(4) is observed in the acids, so that the minor component with this signal at $\delta = 6.86$ has the (2*E*)-con-

Table. *Some spectroscopic properties of bromo-substituted 2-buten- and 2-penten-4-olides*



	2	4	11	13	14	17	20	21
IR.: [a]								
C=O	1755	1758	1795	1770	1760	1800	—	—
C=C	1650	1650	1602	1655	1660	1605	—	—
UV.:								
λ_{max} [b]	213	217	217	—	—	212	—	—
ε	6500	5900	8700	—	—	16400	—	—
^{1}H-NMR.:								
H-C(2) [c]	—	—	6.34(1)	—	—	6.28(1)	—	—
H-C(3)	7.55(1)	7.41(1)	7.77(1)	7.20(1)	6.78(1)	7.55	7.64(1)	7.54(1)
H-C(4)	4.83(2)	5.11(1)	7.05(1)	6.82(1)	5.72(1)	—	—	—
H-C(5)	—	1.53(3)	—	—	—	4.16(2)	2.20(3)	4.20(2)
H-C(1')	4.08(2)	4.11(2)	—	2.00(3)	1.97(3)	—	4.20(2)	4.20(2)
J(2,3) [d]	—	—	6.0	—	—	5.8	—	—
J(2,4)	—	—	0.8	—	—	—	—	—
J(1',3)	1.0	1.5	—	1.7	1.7	—	1.5	1.5
J(1',4)	1.5	1.5	—	1.7	1.7	—	—	—
J(3,4)	2.0	1.5	0.8	1.0	1.0	—	—	—
J(4,5)	—	7	—	—	—	—	—	—

[a]) in cm^{-1}. [b]) in nm. [c]) δ-values (no. of protons). [d]) in Hz.

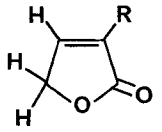
figuration as shown in **8** and the major component (δ = 6.43) the (2*Z*)-configuration as shown in **7**.

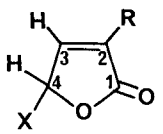
This configurational assignment receives strong support from a new ^{13}C-NMR.-method described by *Vögeli & v. Philipsborn* [9], which uses the observation that the ^{13}C–^{1}H vicinal coupling in trisubstituted olefins is usually larger when these atoms are situated *trans* on a double bond than when they are *cis*. When the carbon atom belongs to a carboxyl group the ratio of *trans*- to *cis*-coupling is about 2, when it is a saturated carbon atom the ratio is about 1.15. The ^{13}C-NMR.-spectrum of the mixture of **7** and **8** shows for the major component a ^{13}COO to ^{1}*H*–C(3) and a ^{13}CH_2Br to ^{1}*H*–C(3) coupling of 5.7 and 8.7 Hz[4]), respectively, but of 10.2 and 6.9 Hz[4]) for the minor component. Thus our *trans*/*cis*-coupling ratios are 1.80 and 1.26, both in good correlation with our configurational assignment.

[4]) Corrected from the observed values by *Pachler's* equation [10]. These values fall slightly outside of the ranges published [9], probably because of the bromine substitution pattern.

Obviously, brominated unsaturated esters differ in their behaviour on treatment with aqueous HBr-solutions: Whereas the 4,1'-dibromo-esters **1** and **3** suffer hydrolysis with lactonization (and therefore isomerization at the double bond), one of the corresponding 4-monobromo-esters [5] and the 4,4,1'-tribromo-esters **5** and **6** undergo only hydrolysis, even though in the case of **6** no double bond isomerization would be required for lactonization.

3. Bromination of lactones. – Treatment of 2-buten-4-olide (**10**) and its 2-methyl derivative **12** [7] with 1 mol-equivalent of N-bromosuccinimide afforded 80% and 30% of 4-bromo-2-buten-4-olide (**11**) and its 2-methyl derivative **13**, respective-





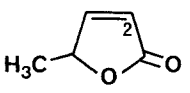
10: R = H
12: R = CH_3

NBS →

11: R = H, X = Br
13: R = CH_3, X = Br
14: R = CH_3, X = OCH_3

ly[5]). The bromo-lactone **13** was converted to the methoxy-lactone **14** by heating in methanol. The structures of the lactones **11**, **13** and **14** are confirmed by their physical properties (see Table and Exper. Part).

The same treatment of 2-penten-4-olide **15** with 1 mol-equivalent of N-bromosuccinimide afforded only a dibrominated product along with recovered educt. A somewhat better yield (34%) of the same product was obtained with 3 mol-equivalents of N-bromosuccinimide. The 4,5-dibromo-2-penten-4-olide structure **17** was assigned to it on the basis of its elemental analysis, mass spectrum and other spectral properties (see Table) as follows: The 2-buten-4-olide ring system was evidenced by



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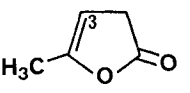

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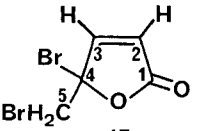
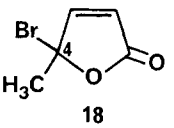


17

the IR.-bands at 1800 and 1605 cm^{-1}, by the UV.-maximum at 212 nm and by the two ^{1}H-NMR.-doublets (J = 5.8) at δ = 6.28 and 7.55 for H–C(2) and H–C(3). The position of the two bromine atoms was confirmed by the AB-system (J = 12) at δ = 4.16 for the two diastereotopic hydrogen atoms at C(5). The same dibromo-lactone **17** resulted (7%) also from 3-penten-4-olide (**16**).

The dibromo-lactone **17** may have been formed by an initial mono-bromination to give **18** (in the case of **16** with allylic isomerization), followed by dehydrobromination to **19** (called protoanemonin) and addition of bromine to the enolic double bond. Both **18** and **19** have been isolated previoulsy [13]. That there may be an

[5] The bromo-lactones **11** and **13** have been prepared previously, **11** by a different method [11] and **13** by the same method as here [2] (compare also [12]).



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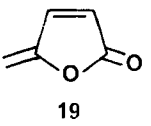

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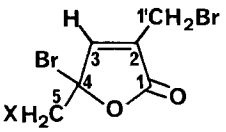
initial mono-bromination of the 2-penten-4-olide system at C(4) was shown in the N-bromosuccinimide treatment of 2-bromomethyl-2-penten-4-olide (**4**), which led to a 2:1 mixture of 4-bromo-2-bromomethyl-2-penten-4-olide (**20**) and 4,5-dibromo-2-



20: X = H
21: X = Br

bromomethyl-2-penten-4-olide (**21**). Here again, the structures of the products have been derived from the physical properties (see Table and Exper. Part).

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Experimental Part

General. The abbreviations and the spectral data notations used here have been described previously [14]. The mass spectra, ^{1}H—NMR.-, ^{13}C—NMR.-spectra and IR.-spectra were measured in our laboratories for mass spectrometry (under Prof. *M. Hesse*), for nuclear magnetic resonance (under Prof. *W. v. Philipsborn* with Mr. *U. Vögeli*) and for micro-analysis (under Mr. *H. Frohofer*), respectively. Elemental analyses were performed in the last mentioned laboratory.

2-Bromomethyl-2-buten-4-olide (**2**). A mixture of 0.4 g (1.6 mmol) of methyl (2*Z*)-4-bromo-2-bromomethyl-2-butenoate (**1**) [5] [6] and 8 ml of 48% HBr solution was heated under reflux for 20–25 min. Water was added and the solution extracted with chloroform. The extracts were washed with water, dried and evaporated to leave 0.144 g (55%) of **2** as an oil, b.p. 80–85°/8 Torr (dec.). – IR. (Film): 1755*s* (C=O), 1650*w* (C=C), 1440*m*, 1350*m*, 1232*m*, 1208*w*, 1070*m*, 1040*m*, 780*w*. – UV. (EtOH): 213 (6500). – ^{1}H-NMR. (100 MHz, $CDCl_3$): 7.55 (*m*, 1 H, H—C(3)), 4.83 (apparent *q*, J = 1.5, 2 H, 2 H—C(4)), 4.08 (apparent *q*, J = 1.5, 2 H, 2 H—C(1′)). – Spin decoupling: Irradiation at 7.55 (H—C(3)) converted the signal at 4.83 (2 H—C(4)) to a *t* (J = 1.5) and the signal at 4.08 (2 H—C(1′)) to a *t* (J = 1.5); irradiation at 4.83 (2 H—C(4)) converted the signal at 7.55 (*H*—C(3)) to a *t* (J = 1.0) and the signal at 4.08 (2 H—C(1′)) to a *d* (J = 1.0); irradiation at 4.08 (2 H—C(1′)) converted the signal at 7.55 (H—C(3)) to a *t* (J = 2.0) and the signal at 4.83 (2 H—C(4)) to a *d* (J = 2.0). – MS. (70 eV): 178 and 176 (3 and 2, M^+), 97 (65, M^+ – Br), 96 (85, M^+ – HBr), 68 (100, M^+ – Br—CO).

$C_5H_5BrO_2$ (177.004): Calc. C 33.93 H 2.85 Br 45.14% Found C 34.44 H 2.98 Br 44.22%

2-Bromomethyl-2-penten-4-olide (**4**). A mixture of 1.0 g (3.5 mmol) of methyl (2*Z*)-4-bromo-2-bromomethyl-2-pentenoate (**3**) [6] and 12 ml of 48% HBr solution was stirred at 90° for 8½–9 h. Work-up as above gave a brown oil which was purified by preparative TLC. on silica gel using ethyl acetate: 0.25 g (37%) of **4** (oil). – IR. (Film): 1758*s* (C=O), 1650*w* (C=C), 1450*w*, 1350*w*, 1320*m*, 1230*w*, 1203*w*, 1138*w*, 1115*w*, 1080*m*, 1025*m*, 950*m*, 788*w*. – UV. (EtOH): 217 (5900). – ^{1}H-NMR. (100 MHz, $CDCl_3$): 7.41 (apparent *q*, J = 1.5, 1 H, H—C(3)), 5.11 (apparent $q \times q$, J = 1.5 and 7, 1 H, H—C(4)), 4.11 (apparent *t*, J = 1.5, 2 H, (2 H—C(1′)), 1.53 (*d*, J = 7, 3 H, 3 H—C(5)). – Spin decoupling: Irradiation at 7.41 (H—C(3)) converted the signal at 5.11 (H—C(4)) to a $t \times q$ (J = 1.5 and 7) and the signal at 4.11 (2 H—C(1′)) to a *d* (J = 1.5); irradiation at 4.11 (2 H—C(1′)) converted the signal at 7.41 (H—C(3)) to a *d* (J = 1.5) and the signal at 5.11 (H—C(4))

to a $d \times q$ (J = 1.5 and 7). – MS. (70 eV): 192 and 190 (1 and 1, M^+), 177 and 175 (3 and 3, $M^+ - CH_3$), 149 and 147 (2 and 2, $M^+ - CH_3$—CO), 111 (100, $M^+ - Br$), 43 (55).

$C_6H_7BrO_2$ (191.03): Calc. C 37.72 H 3.69 Br 41.83% Found C 37.69 H 3.97 Br 41.61%

(2Z)- and (2E)-4,4-dibromo-2-bromomethyl-2-butenoic acid (**7** *and* **8**). The reaction conditions described above were applied to 1 g of a mixture [6] containing ~60% methyl (2Z)-4-bromo-2-bromomethyl-2-butenoate (**1**), ~32% methyl (2Z)- and ~8% methyl (2E)-4,4-dibromo-2-bromomethyl-2-butenoate (**5** and **6**) in 15 ml of 48% HBr solution. The chloroform phases were extracted with a 5% solution of sodium bicarbonate, dried and evaporated to give 0.25 g (~65%) of the *2-bromomethyl-2-buten-4-olide* (**2**). The aqueous extract was acidified with hydrochloric acid and reextracted with chloroform. These extracts were dried and evaporated to give 0.13 g (~34%) of a 4:1 mixture of *(2Z)-4,4-dibromo-2-bromomethyl-2-butenoic acid* (**7**) and *(2E)-4,4-dibromo-2-bromomethyl-2-butenoic acid* (**8**) as an oil, b.p. 90–95°/0.007 Torr, which solidified on standing, m.p. 63–73°. Attempts to separate the two isomers by chromatography or distillation were unsuccessful. – IR. ($CHCl_3$): 3600–2200*s* (br., OH), 1705*s*, (C=O), 1648*w* (C=C), 1605*vw* (C=C), 1420*m*, 1280*m*, 1192*m*. – The ^{1}H—NMR.-spectrum of the mixture is described as if the two isomers were observed separately. ^{1}H—NMR. of **7** (60 MHz, $CDCl_3$): 11.37 (*s*, 1 H, CO_2H), 7.37 (*d*, J = 11, 1 H, H—C(3)), 6.43 (*d*, J = 11, 1 H, H—C(4)), 4.21 (*s*, 2 H, 2 H—C(1')). – ^{1}H—NMR. of **8** (60 MHz, $CDCl_3$): 11.37 (*s*, 1 H, CO_2H), 7.40 (*d*, J = 10.5, 1 H, H—C(3)), 6.86 (br., *d*, J = 10.5, 1 H, H—C(4)), 4.34 (*s*, 2 H, 2 H—C(1')). The separately visible signals for **7** and **8** are all in intensity ratios of 4:1. – The ^{13}C—NMR.-spectrum of the mixture is described in the same manner as the ^{1}H—NMR. (see above). ^{13}C—NMR. of **7** (25.2 MHz, $CDCl_3$): 169.6 (C(1)), 143.8 (C(3)), 125.9 (C(2)), 31.7 (C(4)), 20.2 (C(1')). ^{13}C—NMR. of **8** (25.2 MHz, $CDCl_3$): 168.9 (C(1)), 144.5 (C(3)), 125.0 (C(2)), 34.0 (C(4)), 29.7 (C(1')). Selective decoupling (power of irradiation 278 Hz with offsets of 297 for **7** and 303 for **8**): Irradiation at 4.4 (near the two *s* of 2 *H*—C(1')) converted the more intense signal at 169.6 (C(1) of **7**) to a *d* (J = 4.2) and the less intense signal at 168.9 (C(1) of 8) to a *d* (J = 7.5). Using *Pachler's* equation [10] a coupling constant of 5.7 for **7** and 10.2 for **8** with the ratio *'trans-* to-*cis-*arrangement of COOH to vicinal H' = 1.80 are calculated. Proton-coupled ^{13}C—spectrum: The intense signal centred at 20.2 (C(1') of **7**) and the weak one at 29.7 (C(1') of **8**) both show a small coupling to *H*—C(3) of 8.7 and 6.9 respectively. The ratio of *'trans-*to-*cis-*arrangement of CH_2Br to vicinal H' is 1.26. – MS. (70 eV): 340, 338, 336 and 334 (0.3, 0.6, 0.6 and 0.3, M^+); 295, 293, 291 and 289 (0.4, 0.8, 0.8 and 0.4, $M^+ - CO_2H$); 259, 257 and 255 (39, 78 and 39, $M^+ - Br$); 231, 229 and 227 (15, 30 and 15, $M^+ - Br—CO$); 177 and 175 (100 and 100, $M^+ - Br—HBr$); 149 and 147 (35 and 35, $M^+ - Br—CO—HBr$); 133 and 131 (22 and 22, $M^+ - Br—HBr—CO_2H$); 121 (13); 119 (12); 97 (70, $M^+ - 3 \times Br$); 96 (10).

4-Bromo-2-buten-4-olide (**11**). A mixture of 0.85 g (1.0 mmol) of 2-buten-4-olide (**10**) [7], 2.14 g (1.2 mmol) of recrystallised N-bromosuccinimide and 50 ml of carbon tetrachloride was heated under reflux for 10 min over a 150 W bulb. The mixture was allowed to cool, the succinimide filtered off and the carbon tetrachloride removed under reduced pressure to give after fractional distillation 1.34 g (80%) of **11** as a yellow oil, b.p. 110–120°/11 Torr. – IR. (Film): 1795*s* (C=O), 1602*m* (C=C), 1185*m*, 1145*m*, 1090*s*, 1040*s*, 970*m*, 865*m*, 815*s*, 740*m*. – UV. (EtOH): 217 (8700). – ^{1}H—NMR. (60 MHz, $CDCl_3$): 7.77 (*d* × *d*, J = 0.8 and 6.0, 1 H, H—C(3)), 7.05 (*t*, J = 0.8, 1 H, H—C(4)), 6.34 (*d* × *d*, J = 0.8 and 6.0, 1 H, H—C(2)).

$C_4H_3O_2Br$ (162.98) Calc. C 29.48 H 1.86 Br 49.03% Found C 29.54 H 1.89 Br 49.05%

4-Bromo-2-methyl-2-buten-4-olide (**13**). A mixture of 1 g (1 mmol) of 2-methyl-2-buten-4-olide (**12**) [7], 2.16 g (1.2 mmol) of N-bromosuccinimide and 15 ml of carbon tetrachloride was heated under reflux for 3 h over a 150 W bulb. Isolation of the product as above gave 0.58 g (30%) of **13** as a colourless oil, b.p. 110–118°/12 Torr. – IR. (Film): 1770*s*, (C=O), 1655*m*, (C=C). – ^{1}H—NMR. (100 MHz, $CDCl_3$): 7.20 (*d* × *q*, J = 1.7 and 1.0, 1 H, H—C(3)), 6.82 (*d* × *q*, J = 1.7 and 1.0, 1 H, H—C(4)), 2.00 (*d* × *d*, J = 1.7 and 1.7, 3 H, 3 H—C(1')).

$C_5H_5BrO_2$ (177.004) Calc. C 33.93 H 2.85 Br 45.15% Found C 33.80 H 2.98 Br 43.70%

4-Methoxy-2-methyl-2-buten-4-olide (**14**). A solution of 0.64 g (3.6 mmol) of 4-bromo-2-methyl-2-buten-4-olide (**13**) in 6,5 ml of methanol was heated under reflux for 2 h. The solution was then evaporated under reduced pressure and the residue was fractionally distilled to give 0.31 g (67%) of **14** as a colourless oil, b.p. 70–110°/12 Torr. – IR. (Film): 3010*m*, 2960 m, 2830*m*, 1760*s* (C=O),

1660*m* (C=C). – ^{1}H—NMR. (100 MHz, $CDCl_3$): 6.78 ($d \times q$, J = 1.7 and 1.0, 1 H, H–C(3)), 5.72 ($d \times q$, J = 1.7 and 1.0, 1H, H–C(4)), 3.54 (*s*, 3 H, OCH_3), 1.97 ($d \times d$, J = 1.7 and 1.7, 3 H, 3 H–C(1')).

$C_6H_8O_3$ (128.130) Calc. C 56.24 H 6.29% Found C 56.46 H 5.70%

4,5-Dibromo-2-penten-4-olide (**17**). *a*) *From 2-penten-4-olide* (**15**). A mixture of 0.16 g (1.6 mmol) of **15** [15], 0.92 g (5.2 mmol) of recrystallised N-bromosuccinimide and 15 ml of anhydrous carbon tetrachloride was heated under reflux for 2 h over a 150 W bulb. Isolation of the crude product as above (see **11**) gave 0.3 g of an oil. Purification by preparative TLC. twice on silica gel using chloroform/hexane 7:3 followed by distillation gave 0.14 g (34%) of **17** as a yellow oil, b.p. 60–65°/0.006 Torr. – IR. (Film): 1800*s* (C=O), 1605*m* (C=C), 1420*w*, 1330*m*, 1270*m*, 1235*w*, 1180*m*, 1140*m*, 1070*m*, 1045*m*, 905*s*, 865*m*, 850*m*, 830*s*, 795*w*, 710*w*, 680*m*, 625*m*. – IR. ($CHCl_3$): 1800*s* (C=O), 1605*m* (C=C). – UV. (EtOH): 212 (16400). – ^{1}H—NMR. (60 MHz, $CDCl_3$): 7.55 (d, J = 5.8, 1 H, H–C(3)), 6.28 (*d*, J = 5.8, 1 H, H–C(2)), 4.16 (*AB*, J = 12, 2 H, 2 H–C(5)). – MS. (70 eV): 176 and 174 (4 and 4, M^+ – HBr), 96 (50, M^+ – 2 Br), 68 (80, M^+ – 2 Br–CO), 42 (100).

$C_5H_4Br_2O_2$ (255.91) Calc. C 23.48 H 1.58 Br. 62.45% Found C 23.76 H 1.61 Br 62.29%

When the reaction was attempted with an equimolar amount of N-bromosuccinimide the ^{1}H—NMR.-spectrum of the crude product showed it to be a 1:1 mixture of the starting lactone **15** and the dibromo-lactone **17**

b) *From 3-penten-4-olide* (**16**). Bromination of 0.4 g (4 mmol) of **16** with 1.3 g (7.3 mmol) of N-bromosuccinimide in 20 ml of chloroform/carbon tetrachloride 1:1 was carried out for 17 h as in a). The crude product (0.38 g) was purified by preparative TLC. three times on silica gel using hexane/acetone 7:3, chloroform/carbon tetrachloride 9:1 and hexane/acetone 3:1 followed by distillation to give 0.07 g (7%) of the *dibromo-lactone* **17** whose IR.- and ^{1}H—NMR.-spectra were identical to those described above.

NBS-bromination of 2-bromomethyl-2-penten-4-olide (**4**). Bromination of 0.15 g (0.78 mmol) of **4** with 0.19 g (1.1 mmol) of N-bromosuccinimide in 10 ml of carbon tetrachloride was carried out for 1 1/2 h in the usual way. The crude product (0.2 g) could not be purified due to decomposition. The presence of a 2:1 mixture of *4-bromo-2-bromomethyl-2-penten-4-olide* (**20**) and *4,5-dibromo-2-bromomethyl-2-penten-4-olide* (**21**) was suggested by the ^{1}H—NMR.-spectrum which is described below as if the two components of the mixture were observed separately. – ^{1}H—NMR. of **20** (60 MHz, $CDCl_3$): 7.64 (*t*, J = 1.5, 1 H, H–C(3)), 4.20 *m*, overlapping with the corresponding signal due to **21**, 2 H, 2 H–C(1')), 2.20 (*s*, 3 H, 3 H–C(5)). ^{1}H—NMR. of **21** (60 MHz, $CDCl_3$): 7.54 (*t*, J = 1.5, 1 H, H–C(3)), 4.20 (*m*, part of an *AB* with J = 12 due to 2 H–C(5) is visible, overlapping with the corresponding signal due to **20**, 4 H, 2 H–C(5) and 2 H–C(1'). All separately visible signals due to **20** and **21** are in a 2:1 ratio; the signals due to impurities appear to be less than 10%.

When an equimolar amount of N-bromosuccinimide was used a mixture of the starting lactone **4**, dibromo-lactone **20** and tribromo-lactone **21** was obtained.

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9. The Chemical Ionization of Organic Compounds

1st Communication

Linear Alkenes with Six to Nine Carbon Atoms

by **Raymond Houriet** and **Tino Gäumann**

Department of Physical Chemistry of the EPF, CH–1007 Lausanne, Switzerland

(21. VII. 75)

Summary. The chemical ionization spectra of linear alkenes have been measured using H_2O, CH_4 or CD_3OD as ionizing gas. In the case of 1-heptene the dependence of spectra on pressure, temperature and repeller field strength has been measured and is discussed.

1. Introduction. – The mass spectra of alkenes produced by chemical ionization (CI) with methane as ionizing gas have been described [1]. They are characterized by the formation of the alkenyl ion $(P–1)^+$ by a hydride transfer from the parent olefin $C_nH_{2n}(= P)$. Two homologous series of fragment ions can be observed, the alkyl ions $C_kH_{2k+1}^+$ and the alkenyl ions $C_kH_{2k-1}^+$ ($k < n$). We have now studied the CI spectra using water or methane as ionizing gas, and have found that in the former an intense alkyl peak $C_nH_{2n+1}^+$ is produced by proton transfer from H_3O^+. This work concentrates on the formation and fragmentation of the heptyl ion formed by protonation of 1-, 2- and 3-heptene, and involves the use of D_2O or CD_4 also as ionizing gases. Hexene, octene and nonene have been studied to a lesser extent. We chose to study the formation of alkyl ions by CI because in this case the upper limit of the ion internal energy can be estimated and is relatively small. This is shown by the small degree of fragmentation observed, when these ions are protonated with H_3O^+, the formation of the butyl ion from heptyl ion being the main reaction.

In two preceeding publications we studied the fragmentation of alkyl ions produced from the corresponding halides by electron impact [2] [3]. We showed that fragmentation must be a rather complex reaction, the loss of an alkene as a neutral fragment by direct scission of a C–C bond being a minor reaction. The probability of losing a terminal carbon atom in the neutral fragment is smaller than or equal to the probabilities of losing one or more of the carbon atoms within the chain. In view of the small energy transferred in the protonation reaction, the rate constants for the fragmentation reaction may be considered as analogous to those observed in the metastable decomposition of the ion produced by electron impact. In forthcoming publications in this series [4] we shall discuss the fragmentation of alkyl ions produced by other ion-molecule reactions and the results obtained after ^{13}C labelling.