corrin compounds. Presumably it is the angular methyl group on C(1) that is responsible for the invariant conformation of ring A, but no force-field calculations have been carried out so far to test this suggestion.

One of us (*K.H.*) acknowledges the award of a *NATO*-Postdoctoral Fellowship for the academic year 1972–1973. This work was carried out with the financial support of the *Schweizerischer Nationalfonds zur Förderung der wissenschaftlichen Forschung.*

REFERENCES

[1] *B. Kräutler, A. Pfaltz, R. Nordmann, K.O. Hodgson, J.D. Dunitz & A. Eschenmoser,* Helv. *59,* 924 (1976).
[2] *D. T. Cromer & B. Mann,* Acta crystallogr., Sect. A, *24,* 321 (1968).
[3] *R.F. Stewart, E.R. Davidson & W.T. Simpson,* J. chem. Physics *42,* 3175 (1965).
[4] *J.D. Dunitz & E.F. Meyer, Jr.,* Helv. *54,* 77 (1971).
[5] *M. Currie & J.D. Dunitz,* Helv. *54,* 98 (1971).
[6] *J.L. Hoard,* Science *174,* 1395 (1971).
[7] *L.S. Bartell,* J. Amer. chem. Soc. *81,* 3497 (1959).
[8] *J.D. Dunitz,* Tetrahedron *28,* 5459 (1972).

196. A Specific Synthesis of Ethyl (2*Z*)-2-Bromomethyl-2-butenoate and its Conversion into Mikanecic Ester[1])

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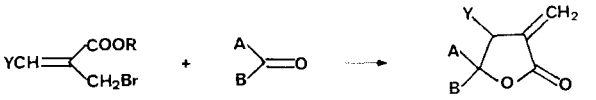
(28. IV. 76)

Eine spezifische Synthese von (2*Z*)-2-Brommethyl-2-butensäure-äthylester und seine Umwandlung in Mikanezester[1]). – *Zusammenfassung.* Das Lithiumsalz **12**, hergestellt aus 2-Bromorthopropensäure-triäthylester (**11**) und *n*-Butyl-lithium, wurde mit Acetaldehyd umgesetzt, wobei 2-Methyliden-3-hydroxy-orthobutansäure-triäthylester (**13**) und daraus, durch saure Hydrolyse, 2-Methyliden-3-hydroxybutansäure-äthylester (**14**) entstand. Behandlung von **14** mit *N*-Bromsuccinimid und Dimethylsulfid lieferte den gewünschten (2*Z*)-2-Brommethyl-2-butensäure-äthylester (**6**), der sich mit HBr zur entsprechenden Säure **4** hydrolysieren liess.

Die (2*Z*)-Konfiguration von **4** wurde aufgrund der *vicinalen* $^1H/^{13}C$ Kopplungen zwischen *H*–C(3) und *C*OOH bzw. *C*H$_2$Br im ^{13}C-NMR.-Spektrum bestätigt. Die ^1H-NMR.-Signale der beiden Methylidenprotonen in **9**, **11**, **13** und **14** liessen sich mit Hilfe von additiven Entschirmungsbeiträgen der Substituenten um die Doppelbindung zuordnen.

1,4-Eliminierung von HBr aus (2*Z*)-2-Brommethyl-2-butensäure-äthylester (**6**) mit Kalium-*t*-butylat ergab Mikanezsäure-diäthylester (**21**), der bei der Aufarbeitung teilweise zum Monoester **20** und zur Mikanezsäure[1]) (**19**) verseift wurde.

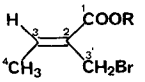
1. Introduction. – Some years ago it was discovered [1] that β-bromoesters of type **1** react readily with carbonyl compounds **2** under *Reformatsky* conditions to give α-methylidene-γ-butyrolactones (**3**). The reaction was found with methyl (2*Z*)-

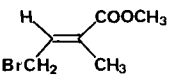


1 **2** **3**

[1]) The systematic name for mikanecic acid (**19**) is 4-vinyl-1-cyclohexene-1,4-dicarboxylic acid.
[2]) Postdoctoral Fellow, 1974–1976.

2-bromomethyl-2-butenoate (**5**). This compound had been obtained as the minor product from the *N*-bromosuccinimide bromination of methyl (2*Z*)- or (2*E*)-2-methyl-2-butenoate along with the major product, methyl (2*E*)-2-methyl-4-bromo-2-butenoate (**7**) [2]. The separation of the two bromoesters **5** and **7** had been achieved only with difficulty. Recently a stereoselective synthesis of (2*E*)-2-methyl-4-halo-2-butenoates similar to **7** has been published [3]. We here report a specific synthesis of





4 R = H

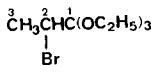
5 R = CH_3

6 R = C_2H_5

7

ethyl (2*Z*)-2-bromomethyl-2-butenoate (**6**) using a concept similar to that described for the preparation of (2*Z*)-2-chloromethyl-2-butenal [4].

2. Preparation of (2*Z*)-2-bromomethyl-2-butenoic acid (4). – Triethyl 2-bromo-orthopropenoate (**11**) was prepared according to the described procedure [5] *via* **8**, **9** and **10** with slight modifications. The lithium salt **12**, obtained by treatment



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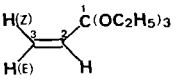

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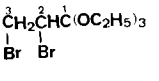

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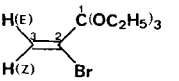

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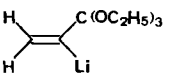
of **11** with butyl lithium, was condensed with acetaldehyde to give triethyl 2-methylidene-3-hydroxy-orthobutanoate (**13**; 82%), which was hydrolysed in a two-phase system to ethyl 2-methylidene-3-hydroxy-butanoate (**14**; 91%). Treatment with



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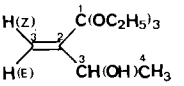

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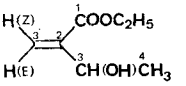
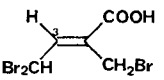


14

N-bromosuccinimide and dimethyl sulfide [4] [6] converted **14** into the desired ethyl (2*Z*)-2-bromomethyl-2-butenoate (**6**; 87%). Hydrolysis of **6** with 48% aqueous HBr afforded the corresponding acid **4** in **85**% yield, m.p. 111–112.5° [2].



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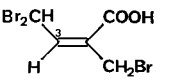


16

3. Configuration of (2*Z*)-2-bromomethyl-2-butenoic acid (4). – Previously the assignment of the (2*Z*)-configuration to **4** was based on comparison of the ^{1}H-NMR.

chemical shifts of H–C(3) and H_3–C(4) with those of equivalent protons in similar compounds [2]. A recent observation suggested caution with one of the arguments used, namely the one which said that a chemical shift of $\delta = 7.25$ for H–C(3) in **4** indicated a *cis* arrangement between this proton and the carboxyl group, assuming that a *trans* arrangement required a lower δ-value for H–C(3)[3]. This observation was that the stereoisomeric tribromoacids **15** and **16** showed very similar chemical shifts for H–C(3) ($\delta = 7.37$ and 7.40) [9]. However, the previous configurational assignment for **4** is now supported by ^{13}C-NMR. measurements: The *vicinal* $^1H/^{13}C$ coupling constants for H–C(3) are $J_{H-C(3)/C(1)} = 5.4$ and $J_{H-C(3)/C(3')} = 9$, visible in the signals at $\delta = 171.0$ (C(1)) and 23.2 (C(3')). This suggests a *cis* location for *H*–C(3) and –*C*O_2H as well as a *trans* arrangement for *H*–C(3) and –*C*H_2Br [10], both of which correspond with a (2*Z*)-configuration of **4**.

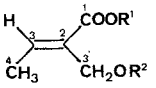
4. Assignment of ^{1}H-NMR. signals to protons at terminal double bonds. – The following is an attempt to assign the ^{1}H-NMR. signals (CCl_4-solutions) in the $\delta = 5.3$–7.0 region of the propenoate (**14**) and orthopropenoate derivatives (**9**, **11** and **13**). The signals of orthoester **9** are assigned from the coupling pattern (similar to that known for ethyl propenoate [11]), analysed by spin simulation as an *ABX*-system, as follows: $\delta = 5.57$ ($J = 10$ and 17) to H–C(2), $\delta = 5.45$ ($J = 2.4$ and 17) to H(*Z*)–C(3) and $\delta = 5.29$ ($J = 2.4$ and 10) to H(*E*)–C(3) (for the signification of H(*Z*) and H(*E*) see the formula). According to the concept of *Pasqual et al.* [7] [8] (see also [12]), the following three approximate deshielding increments Z are calculated from these values for the –C(OC_2H_5)$_3$ (orthoester) group as a substituent on a double bond: $Z_{gem} = 0.32$, $Z_{cis} = 0.20$ and $Z_{trans} = 0.04$ ppm.

Using these values of Z_{cis} and Z_{trans} along with the corresponding increments given in [8] for –Br the signals of the bromo-orthoester **11** are assigned as follows: $\delta = 5.78$ to H(*Z*)–C(3) and $\delta = 6.22$ to H(*E*)–C(3) (calc. 5.74 and 6.00, respectively). Since the two signals for the two H–C(3') in the hydroxy-orthoester **13** are quite similar in chemical shift ($\delta = 5.45$ and 5.33) they are not assigned individually. However, using the two possible assignements of these signals, *i.e.* $\delta = 5.45$ to H(*E*) and $\delta = 5.33$ to H(*Z*) of **13**, or *vice versa*, one can calculate two of the three deshielding increments Z for the –CH(OH)CH_3 group: accordingly Z_{cis} amounts to 0.04 or 0.16 ppm, and Z_{trans} to 0.00 or –0.12 ppm. These values together with the literature values for –COOR [8] can be used to assign signals in the hydroxy-ester **14** as follows: $\delta = 6.17$ to H(*Z*)–C(3') (calc. 6.43 or 6.31) and $\delta = 5.85$ to H(*E*)–C(3') (calc. 5.84 or 5.96). In a similar manner assignments for the previously reported [2] hydroxy acid corresponding to **14** can be made: in $CDCl_3$ $\delta = 6.37$ is attributed to H(*Z*)–C(3') (calc. 6.66 or 6.54) and $\delta = 5.93$ to H(*E*)–C(3') (calc. 6.00 or 6.12).

5. Conversion to mikanecic acid and its ethyl esters. – The observation that structural units such as serracinic acid (= (2*E*)-2-hydroxymethyl-2-butenoic acid; **17**) may be precursors for the formation of mikanecic acid[1]) (**19**) has been

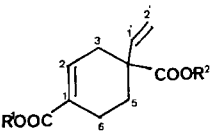
[3]) A more precise analysis can be made with the help of deshielding increments by the method of *Pascual et al.* [7] [8]. The observed δ-values for H–C(3) in **4** and **6** (7.25 and 7.05) fit better for the (2*Z*)-configuration, as expressed in formulae **4** and **6** (calc. 7.07 and 6.84), than for the corresponding (2*E*)-isomers (calc. 6.52 and 6.36).

mentioned previously [13] [14]. Methyl mikanecate has also been isolated as a minor by-product of the saponification of the mixture of the bromoesters **5** and **7** (after reesterification with diazomethane) [2]. It was implied that **5** was the more probable precursor for isoprenic acid [2] which dimerized to mikanecic acid (**19**). The implication appeared reasonable, because 1,4-elimination of HBr from **5** involves depro-



17 $R^1 = R^2 = H$

18 $R^1 = C_2H_5$, $R^2 = C(CH_3)_3$



19 $R^1 = R^2 = H$

20 $R^1 = H$, $R^2 = C_2H_5$

21 $R^1 = R^2 = C_2H_5$

tonation from an activated position (vinylogous to the ester group). We now confirm this point by isolating compounds having the mikanecic acid structure in about 50% yield from the treatment of ethyl (2*Z*)-2-bromomethyl-2-butenoate (**6**) with potassium *t*-butoxide[4]). The work-up procedure brought about partial saponification, so that a mixture of diethyl mikanecate (**21**, 33%), monoethyl mikanecate (**20**, 9%), and mikanecic acid (**19**, about 15%) was obtained. A minor by-product (4%) from this reaction was ethyl (2*E*)-2-*t*-butoxymethyl-2-butenoate (**18**).

This work was supported by the *Schweizerischer Nationalfonds zur Föderung der wissenschaftlichen Forschung* and by *Sandoz AG*, Basel. We thank Mr. *W. Schwotzer* for spin simulation and Mr. *U. Vögeli* for ^{13}C-NMR. measurements.

Experimental Part

General. See [9] [14].

Triethyl 2-bromo-orthopropanoate (**8**). For procedure see [5], yield 77%, b.p. 80–82°/10 Torr. – IR. (CCl_4): 2980*s*, 2940*m*, 2900*m*, 2870*m* sh, 1485*w*, 1458*m*, 1448*m*, 1393*m*, 1377*m*, 1369*m*, 1325*m*, 1225*s*, 1210*s* sh, 1160*m*, 1115*s*, 1095*s* sh, 1080*s* sh, 1065*s*, 1020*m*, 980*m*, 670*w*, 650*m*. – ^1H-MNR. (100 MHz, CCl_4): 1.17 (X_3 part of ABX_3, $J_{AX} \cong J_{BX} \cong 7.2$, 9H, 3 CH_3CH_2O); 1.67 (*d*, $J = 7$, 3H, 3H–C(3)); 3.59 (*B* part of ABX_3, $J_{BA} = 9.5$, $J_{BX} \cong 7.2$, 3 $CH_3-CH_AH_B-O$) and 3.70 (*A* part of ABX_3, $J_{AB} = 9.5$, $J_{AX} \cong 7.2$, 3 $CH_3-CH_AH_B-O$) (together 6H); 4.09 (*q*, $J = 7$, 1H, H–C(2)).

Triethyl orthopropenoate (**9**). For procedure see [5] (commercial potassium *t*-butoxide was used), yield 73%, b.p. 74–74.5°/29 Torr. – IR. (CCl_4): 3100*w*, 3035*w*, 2985*s*, 2935*s*, 2900*s*, 2880*m* sh, 1485*w*, 1460*w*, 1450*m*, 1410*s*, 1390*m*, 1370*w*, 1290*w*, 1220*s*, 1175*s* sh, 1160*s* sh, 1070*vs* br., 1050*s* sh, 990*s*, 945*s*. – ^1H-NMR. (100 MHz, CCl_4): 1.13 (*t*, $J = 7$, 9H, 3 CH_3CH_2O), 3.40 (*q*, $J = 7$, 6H, 3 CH_3CH_2O), 5.19–5.72 (*ABX* pattern, 3H); simulation gives 5.29 for *X* part, $J_{XB} = 2.4$, $J_{XA} = 10.0$ (H(*E*)–C(3)), 5.45 for *B* part, $J_{BA} = 17.0$, $J_{BX} = 2.4$ (H(*Z*)–C(3)), 5.57 for *A* part, $J_{AB} = 17.0$, $J_{AX} = 10.0$ (H–C(2)).

Triethyl 2,3-dibromo-orthopropanoate (**10**). The bromination of 6.96 g (40 mmol) of **9** according to [5] was performed at –30° in the presence of CaO to prevent acid hydrolysis of the ortho ester. The crude residue, which still contained CaO, was used directly for the next step described in the following experiment. A sample was treated with carbon tetrachloride and filtered for

[4]) This result has been preliminarily mentioned in footnote [7]) of [14].

NMR. measurement. – ^{1}H-NMR. (60 MHz, CCl_4): 1.33 (X_3 part of ABX_3, $J_{AX} \cong J_{BX} \cong 7$, ~9H, 3 CH_3CH_2O), 3.1–4.6 (*m* including signal at 3.72, AB part of ABX_3, $J_{AX} \cong J_{BX} \cong 7$, ~9H, 3 CH_3CH_2O, H–C(2) and 2 H–C(3)); signals corresponding to about 10% of **11** were also present.

Triethyl 2-bromo-orthopropenoate (**11**). The crude residue obtained in the preceding experiment (which contained up to 36 mmol of triethyl 2,3-dibromo-orthopropanoate (**10**) and up to 4 mmol of triethyl 2-bromo-orthopropenoate (**11**)) was treated with a solution of 2.80 g (50 mmol) of KOH in 25 ml of absolute ethanol. After stirring during 20 h, 100 ml of ether were added and the mixture was filtered through Celite. The filtrate was washed with saturated NaCl solution, dried over K_2CO_3, evaporated and distilled to give 7.89 g (78% from **9**) of **11** as a colourless oil, b.p. 57–60°/1 Torr. – IR. (CCl_4): 2985*s*, 2935*m*, 2905*m*, 2875*w* sh, 1630*w*, 1485*w*, 1460*w*, 1448*w*, 1395*w*, 1375*w*, 1340*w*, 1225*s*, 1160*m* sh, 1118*s*, 1100*s* sh, 1065*s*, 1050*s* sh, 1025*m* sh, 920*m*, 875*w*, 685*w*. – ^{1}H-NMR. (60 MHz, CCl_4): 1.20 (*t*, J = 7, 9H, 3 CH_3CH_2O); 3.43 (*q*, J = 7, 6H, 3 CH_3CH_2O); 5.78 (*d*, J = 1.5, 1H, H(*Z*)–C(3)); 6.22 (*d*, J = 1.5, 1H, H(*E*)–C(3)).

Triethyl 2-methylidene-3-hydroxy-orthobutanoate (**13**). To a stirred solution of 1.265 g (5 mmol) of triethyl 2-bromo-orthopropenoate **11** in 25 ml of dry tetrahydrofuran were added, during 30 min at –75°, 2.3 ml of a 2.2N *n*-butyl lithium solution in hexane (~5mmol). After 0.5 h a solution of 0.78 g (17.7 mmol) of acetaldehyde in 5 ml of tetrahydrofuran was added during 30 min at –75°. The solution was stirred for 0.5 h, allowed to warm to RT., and treated with saturated NaCl solution and ether. The organic layer was washed with saturated NaCl solution until neutral, dried over K_2CO_3, and evaporated. Distillation of the residue afforded 900 mg (82%) of **13** as a colourless oil, b.p. 80°/9 Torr (bulb to bulb distillation). – IR. (CCl_4): 3620*w*, 3550*w*, 2985*s*, 2935*m*, 2905*m*, 2880*w* sh, 1485*w*, 1460*w* sh, 1450*m*, 1395*m* br., 1370*w*, 1300*w*, 1265*m*, 1180*m* sh, 1150*s* sh, 1130*s* sh, 1115*s* sh, 1070*s* br., 940*m*, 920*w*, 900*w*. – ^{1}H-NMR. (60 MHz, CCl_4): 1.17 (*t*, J = 7.5, 3CH_3CH_2O) and 1.23 (*d*, J = 6.5, 3H–C(4)) (together 12H); 2.88 (*d*, J = 3.5, 1H, OH); 3.45 (*q*, J = 7.5, 6H, 3CH_3CH_2O); 4.30 (*q* × *d* with broadened lines, J = 6.5 and 3.5, 1H, H–C(3)); 5.33 (*d*, J = 2, 1H, H–C(3')); 5.45 (*d* × *d*, J = 2 and 1.5, 1H, 1H–C(3')). After addition of D_2O: 2.88 absent, 4.30 (*q* with broadened lines, J = 6.5). – MS. (70 eV): 173 (9, $M-C_2H_5O$), 147 (8, $M-C_4H_7O$), 129 (11, $M-C_2H_5O-C_2H_4O$), 127 (22, $M-C_2H_5O-C_2H_4-H_2O$), 119 (10, $M-C_4H_7O-C_2H_4$), 101 (19, $M-C_2H_5O-C_2H_4O-C_2H_4$), 100 (9), 99 (37, $M-C_2H_5O-C_2H_4-H_2O-C_2H_4$), 98 (26), 97 (15), 91 (15, $M-C_4H_7O-C_2H_4-C_2H_4$), 83 (37, $M-C_2H_5O-C_2H_4O-C_2H_4-H_2O$), 82 (12), 81 (34, $M-C_2H_5O-C_2H_4-H_2O-C_2H_4-H_2O$), 73 (12, $M-C_4H_7O-C_2H_4-C_2H_4-H_2O$), 72 (5), 71 (9), 70 (8), 69(12), 63 (20, $M-C_4H_7O-C_2H_4-C_2H_4-C_2H_4$), 56 (9), 55 (61), 54 (25), 53 (35), 52 (12), 51 (12), 50(10), 46 (27), 45 (100), 44 (83), 43 (71), 42 (20), 41 (14).

$C_{11}H_{22}O_4$ (218.297) Calc. C 60.52 H 10.16% Found C 60.20 H 10.21%

Ethyl 2-methylidene-3-hydroxybutanoate (**14**). A solution of 981 mg (4.5 mmol) of triethyl 2-methylidene-3-hydroxy-orthobutanoate (**13**) in 10 ml of ether was stirred during 0.5 h with 10 ml of 0.25N aqueous H_2SO_4. The aqueous layer was extracted with ether and the combined organic solutions were washed with 5% $NaHCO_3$ solution and with saturated NaCl solution, dried over K_2CO_3, and evaporated. Distillation of the residue afforded 590 mg (91%) of **14** as a colourless oil, b.p. 70°/9 Torr (bulb to bulb distillation). – IR. (CCl_4): 3615*w*, 3540*m*, 2985*s*, 2940*m*, 2910*m*, 2875*w*, 1710*s* br., 1632*m*, 1480*m*, 1468*m*, 1450*m*, 1400*m* br., 1373*s*, 1328*s*, 1295*s* br., 1270*s*, 1175*s*, 1155*s*, 1090*s*, 1040*m* sh, 1030*s*, 955*s*, 930*m*, 900*m*, 865*w*. – ^{1}H-NMR. (60 MHz, CCl_4): 1.25 (*d*, J = 6.5, 3H–C(4)) and 1.28 (*t*, J = 7.5, CH_3CH_2O) (together 6H); 3.33 (*d*, J = 4.5, 1H, OH); 4.20 (*q*, J = 7.5, CH_3CH_2O) and 4.57 (*m*, H–C(3)) (together 3H); 5.85 (*t*, J = 1.5, 1H, H(*E*)–C(3')); 6.17 (finely split *s*, 1H, H(*Z*)–C(3')). On addition of D_2O: 3.33 absent; 4.57 (*q*, J = 6.5). – MS. (70 eV): 129 (48, $M-CH_3$), 115 (7, $M-C_2H_5$), 101 (71, $M-CH_3-C_2H_4$), 99 (41, $M-C_2H_5O$), 98 (35), 97 (21), 87 (6), 84 (6), 83 (100, $M-CH_3-C_2H_4-H_2O$), 82 (5), 81 (31), 73 (33, $M-C_4H_7O$), 72 (7), 71 (23), 70 (18), 69 (8), 56 (9), 55 (48, $M-C_2H_5O-C_2H_4O$), 54 (13), 53 (19), 45 (26, $M-C_4H_7O-C_2H_4$), 44 (14), 43 (40), 42 (5), 41 (10).

$C_7H_{12}O_3$ (144.173) Calc. C 58.32 H 8.39% Found C 57.98 H 8.63%

Ethyl (2Z)-2-bromomethyl-2-butenoate (**6**) *and (2Z)-2-bromomethyl-2-butenoic acid* (**4**). To a solution of 2.160 g (12 mmol) of *N*-bromosuccinimide in 40 ml of dry methylene chloride was added at 0° under N_2 a solution of 933 mg (15 mmol) of dimethyl sulfide in 4 ml of methylene chloride

while a yellow solid separated. A solution of 576 mg (4 mmol) of ethyl 2-methylidene-3-hydroxybutanoate (**14**) was added, and the mixture was stirred at RT. during 6 h. It was then diluted with cold pentane, and poured into cold saturated NaCl solution. The aqueous phase was extracted with pentane, and the combined organic extracts were washed with saturated NaCl solution, dried over $MgSO_4$, and evaporated. Distillation of the residue at 40°/0.1 Torr afforded 721 mg (87%) of ^{1}H-NMR. pure **6**. – IR. (CCl_4): 2990*m*, 2970*w* sh, 2940*w*, 2910*w*, 2875*w*, 2850*w*, 1723*s*, 1653*m*, 1480*w*, 1448*m*, 1385*m*, 1370*m*, 1352*w*, 1280*s* sh, 1272*s*, 1220*m*, 1175*s*, 1162*s*, 1128*m*, 1098*w*, 1055*m*, 1025*w*, 870*w*, 670*w*. – ^{1}H-NMR. (60 MHz, CCl_4): 1.32 (*t*, J = 7.5, 3H, CH_3CH_2O); 1.93 (*d*, J = 7.5, 3H, 3H–C(4)); 3.87 (*s*, 2H–C(3′)) and 3.90 (*q*, J = 7.5, CH_3CH_2O) (together 4H); 7.05 (*q*, J = 7.5, 1H, H–C(3)).

A mixture of this ester and 8 ml of 48% aqueous HBr was heated under reflux during $^1/_2$ h, cooled and extracted with ether. The ethereal solution was dried over $MgSO_4$, and evaporated, and the residue was recrystallized from ether/pentane to give 530 mg (85%) of *(2Z)-2-bromomethyl-2-butenoic acid* (**4**), m.p. 111–112.5°, with spectral data identical to those previously reported [2]. ^{13}C-NMR. (25.2 MHz, $CDCl_3$): 171.0 (C(1)); 145.9 (C(3)); 129.7 (C(2)); 23.2 (C(3′)); 14.8 (C(4)). – Proton coupled ^{13}C-spectrum: the signal at 23.2 appears as $d \times t$ (J = 9 and 155) and the signal at 171.0 as $d \times t$ (J = ~5.4 and 5). – Selective decoupling: Irradiation at 4.25 ($H_2C(3')$) converted the signal at 171.0 into *d* (J = 5.4)[5]. Thus $J_{C(1)/H-C(3)} = 5.4$ and $J_{C(3')/H-C(3)} = 9$.

4-Vinyl-1-cyclohexene-1,4-dicarboxylic acid (*mikanecic acid*) (**19**), *its monoethyl* (**20**), *and diethyl esters* (**21**). To a solution of 497 mg (2.4 mmol) of ethyl (2*Z*)-2-bromomethyl-2-butenoate (**6**) in 10 ml of *t*-butyl alcohol were added 336 mg (3 mmol) of potassium *t*-butoxide. The mixture was stirred during 5 h and then treated with ether and saturated NaCl solution. The basic aqueous layer was extracted with more ether, the combined organic extracts were washed with saturated NaCl solution, dried over $MgSO_4$, and evaporated to give 244 mg of an oil. The work-up of the combined aqueous layers will be described below. Purification by thick layer chromatography of the residue from the organic layer using pentane/ether 2:1 gave 138 mg which consisted mainly of **21** (according to ^{1}H-NMR.). Rechromatography with hexane/acetone 5:1 gave two fractions, the less polar of which contained 30 mg of a colourless oil with an ^{1}H-NMR. spectrum corresponding to ethyl *(2E)-2-t-butoxymethyl-2-butenoate* (**18**) (yield ~4%). – IR. (CCl_4): 2985*s*, 2930*m*, 2905*m*, 2870*m*, 1715*s*, 1658*m*, 1480*m*, 1460*m* sh, 1445*m*, 1400*w* sh, 1385*m*, 1375*m*, 1362*s*, 1335*w*, 1280*s*, 1230*s*, 1192*s*, 1170*m*, 1155*m* sh, 1137*s*, 1090*m*, 1060*s*, 1022*m*, 950*w*, 895*m*. – ^{1}H-NMR. (60 MHz, CCl_4): 1.18 (*s*, $(CH_3)_3C-O$) and 1.25 (*t*, J = 7, CH_3CH_2O) (together ~12H); 1.87 (*d*, J = 7.5, 3H, 3H–C(4)); 4.03 (*s*, 2H–C(3′)) and 4.12 (*q*, J = 7, CH_3CH_2O) (together 4H); 6.92 (*q*, J = 7.5, 1H, H–C(3)); some additional signals due to a slight impurity were present in the 1 ppm region.

The more polar fraction was purified by bulb to bulb distillation at 55°/0.005 Torr to give 102 mg (33%) of *diethyl 4-vinyl-1-cyclohexene-1,4-dicarboxylate* (**21**, *diethyl mikanecate*) as a colourless oil, with ^{1}H-NMR. and IR. spectra in agreement, as far as reported, with those described previously [14]. – ^{1}H-NMR. (60 MHz, CCl_4): 5.07 ($d \times d$, J = 1.2 and 18.5, H(*Z*)–C(2′)) and 5.10 ($d \times d$, J = 1.2 and 10, H(*E*)–C(2′)) (together 2H); 5.92 ($d \times d$, J = 10 and 18.5, 1H, H–C(1′)); 6.88 (*m*, with visible splitting of 2, 1H, H–C(2)); for the rest of the signals see [14].

The combined aqueous layers were acidified with concentrated HCl to pH ~1 and extracted with ether. The extract was washed with saturated NaCl solution until neutral, dried over $MgSO_4$, and evaporated to give 101 mg of a solid residue. Thick layer chromatography using ether/pentane 3:1 as eluant afforded 25 mg (9%) of crude *4-ethoxycarbonyl-4-vinyl-1-cyclohexene-1-carboxylic acid* (**20**, *ethyl mikanecate*) as a colourless solid, after recrystallization from ether/pentane, m.p. 110–112°. – IR. (CCl_4): 3600–2300*m*, 1722*s*, 1690*s*, 1650*m*, 1425*m* br., 1365*w*, 1277*m*, 1258*m* sh, 1215*m* br. sh, 1175*m* sh, 1090*m* br., 1020*w*, 922*w*. – ^{1}H-NMR. (100 MHz, $CDCl_3$): 1.23 (*t*, J = 7, 3H, CH_3CH_2O), 1.5–3.1 (*m*, 6H, 2H–C(3), 2H–C(5), 2H–C(6)); 4.14 (*q*, J = 7, 2H, CH_3CH_2O); 5.11 (*d*, J = 17.5, H(*Z*)–C(2′)) and 5.17 (*d*, J = 11, H(*E*)–C(2′)) (together

[5] The power of irradiation was 450 Hz with offset of 300. The coupling constant was corrected using *Pachler*'s equation [15].

2H); 5.91 ($d \times d$, J = 11 and 17.5, 1H, H–C(1')); 7.1 (m, 1H, H–C(2)). – MS. (70 eV): 224 (24, M), 206 (25, $M-H_2O$), 178 (7), 152 (13), 151 (100, $M-CO_2C_2H_5$), 150 (27), 149 (7), 134 (6), 133 (43, $M-CO_2C_2H_5-H_2O$), 132 (7), 123 (9), 107 (6), 106 (7), 105 (42), 104 (6), 103 (6), 98 (9), 91 (17), 79 (21), 78 (7), 77 (15).

Elution of the more polar fraction gave 26 mg of a colourless solid which according to its ^{1}H-NMR. spectrum [14] consisted mainly of *4-vinyl-1-cyclohexene-1,4-dicarboxylic acid* (**19**, *mikanecic acid*), the impurities giving rise to signals in the 1–1.5 ppm region, yield up to 15%. Recrystallization from ether/pentane gave a colourless solid, m.p. ~225°, lit. [14] m.p. 239–240°.

REFERENCES

[1] *A. Löffler, R. J. Pratt, J. Pucknat, G. Gelbard & A. S. Dreiding*, Chimia *23*, 413 (1969).
[2] *A. Löffler, R. J. Pratt, H. P. Rüesch & A. S. Dreiding*, Helv. *53*, 383 (1970).
[3] *P. L. Stotter & K. A. Hill*, Tetrahedron Letters *1975*, 1679.
[4] *J. C. Depezay & Y. Le Merrer*, Tetrahedron Letters *1974*, 2751.
[5] *H. Stetter & W. Uerdingen*, Synthesis *1973*, 207.
[6] *E. J. Corey, C. U. Kim & M. Takeda*, Tetrahedron Letters *1972*, 4339.
[7] *C. Pascual, J. Meier & W. Simon*, Helv. *49*, 164 (1966).
[8] *U. E. Matter, C. Pascual, E. Pretsch, A. Pross, W. Simon & S. Sternhell*, Tetrahedron *25*, 691 (1969).
[9] *C. B. Chapleo, K. L. Svanholt, R. Martin & A. S. Dreiding*, Helv. *59*, 100 (1976).
[10] *U. Vögeli & W. v. Philipsborn*, Org. magn. Res. *7*, 617 (1975).
[11] *W. Brügel, Th. Ankel & F. Krückeberg*, Z. Elektrochem. *64*, 1121 (1960).
[12] *S. W. Tobey*, J. org. Chemistry *34*, 1281 (1969).
[13] *C. C. J. Culvenor & T. A. Geissman*, Chemistry & Ind. *1959*, 366; *idem*, J. org. Chemistry *26*, 3045 (1961).
[14] *L. K. Sydnes, L. Sakttebøl, C. B. Chapleo, D. G. Leppard, K. L. Svanholt & A. S. Dreiding*, Helv. *58*, 2061 (1975).
[15] *K. G. R. Pachler*, J. magn. Res. *7*, 442 (1972).

Errata

Helv. *58*, 969 (1975), Abhandlung Nr. 163 von *L. Baláspiri, B. Penke, Gy. Papp, G. Dombi* und *K. Kovács*: auf S. 972, 6. Zeile von oben: anstatt $C_{26}H_{41}N_2O_4$ (445,59) lies $C_{26}H_{40}N_2O_4$ (444,60).

Helv. *59*, 1018 (1976), Abhandlung Nr. 107 von *W. Stegmann, P. Gilgen, H. Heimgartner* und *H. Schmid*, Schema 4 und Fussnote 9, S. 1022: Die Formel **10d** entspricht nicht der im Text angegebenen (*E*)-Konfiguration. H und H_5C_2O an C(1') sind demnach in Formel **10d** zu vertauschen.